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STATE OF CALIFORNIA

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MINERALS USEFUL TO CALIFORNIA AGRICULTURE

PREPARED UNDER THE DIRECTION OF OLAF P. IENKINS



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PREFACE

That the soil represents a mineral resource is seldom realized by the Mineral Industry, but this most important of nature's rock products is placed in the category of the Agricultural Industry. The soil scientist is one of the best mineralogists of clay materials, the agricultural chemist contributes immeasurably to the chemical evaluation of the mineral materials which are added to the soil to benefit it, and the soil surveyor uses the knowledge of geological processes to determine the origin of the soil he is mapping.

A more commercial aspect of the soil, so far as the miner is concerned, lies in the market for mineral materials which is developed by the Agricultural Industry in its demand for such materials to be used in benefiting the soil, either as a fertilizer or as a conditioner. The market extends even farther into uses of minerals as insecticides and insecticide earriers.

To market minerals intelligently, to contribute minerals where they are actually needed, and to represent truthfully the product marketed, places upon the miner the responsibility of knowing something of the nature of soil and its needs and to appreciate his contribution. To utilize minerals intelligently where they are actually needed in agriculture, to know the exact composition and nature of the minerals used, and to realize where these minerals can be obtained and in what form they may be secured, places a responsibility upon the farmer who contributes to the livelihood and health of our civilization.

It is the aim of this book, therefore, to present to the reader the facts concerning the various soils of California and their needs, the mineral materials which are sold to and used by agriculture today, and the sources of supply in this State of many of these minerals now used.

It is hoped that on the one hand, this initial step will encourage the agriculturalist to learn more of the geology and mineral resources of California. On the other hand, it is hoped that the producer of minerals will realize the importance of contributing minerals for the soil, thereby increasing the agricultural wealth of the State and its Mineral Industry.

The reader may be assured of the authenticity of the contents of this bulletin, since it represents the joint product of disinterested technical personnel of the State's divisions of Soil, Chemistry, and Mines.

> OLAF P. JENKINS Chief, Division of Mines

San Francisco January 5, 1951



EXPLORING THE SOILS OF CALIFORNIA +

BY HANS JENNY AND COLLABORATORS *

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[†] Reprinted from *California Agriculture*. University of California Press, 1946. ^{*} The following members of the Agricultural Experiment Station have made specific contributions to this survey: Frank Adams, D. I. Arnon, G. B. Bodman, T. C. Broyer, J. P. Conrad, W. P. Kelley, R. E. Storie, Albert Ulrich, F. J. Veihmeyer, W. W. Weir. Footnotes one to fourteen in this issue have been added by H. Jenny in 1950, after consultation with collaborators.

Such knowledge of soils and soil-management methods as was brought to California by early settlers from the humid East and from western Europe often proved of questionable value in the arid and semiarid regions of the state. Prolonged seasons of drought and the frequent occurrence of soil alkali presented unfamiliar and serious obstacles to the agricultural immigrant. Later, the shift from large-scale dry farming to specialized crops and orchards under irrigation brought to light many unforeseen problems and threw new tasks upon soil scientists.

California soil-research achievements of the past 70 years are impressive. Still to be solved, however, is a bewildering array of problems, both

| No. | Area | Date of survey | No. | Arca | Date of survey |
|-----------------|---------------------------------|----------------------|------|---------------------|----------------------|
| | Around Fresno* | 1900 | 31 | Lancaster | 1922 |
| | Around Santa Ana* | 1900 | 32 | Palo Verde | 1922 |
| | llanford* | 1901 | - 33 | Coachella Valley | 1923 |
| | Soledad Sheet* | 1901 | 34 | Gilroy | 1923 |
| | Lower Salinas Valley* | 1901 | 35 | Hollister | 1923 |
| | Ventura* | 1901 | 36 | Auburn | 1923 |
| | San Gabriel* | 1901 | 37 | Bishop | 1924 |
| | Imperial Valley* | 1901 | - 38 | King City | 1924 |
| | San Jose* | 1903 | - 39 | Chico | 1925 |
| | Imperial* | 1903 | 40 | Salinas | 1925 |
| | Indio* | 1903 | 41 | Oroville | 1926 |
| | Los Angeles* | 1903 | 42 | Clear Lake | 1927 |
| | Bakersfield* | 1904 | -43 | Placerville | 1926 |
| | Sacramento* | 1904 | 44 | Santa Ynez | 1927 |
| | Yuma Area, Arizona-California*_ | 1904 | 45 | Paso Robles* | 1928 |
| | San Bernardino Valley* | 1904 | 46 | San Luis Obispo | 1928 |
| | Stockton* | 1905 | 47 | Capistrano* | 1929 |
| 3 | Colusa* | 1907 | 48 | Oceanside* | 1929 |
| 4 | Redding* | 1907 | 49 | El Cajon* | 1929 |
| | Klamath Reclamation Project* - | 1908 | 50 | Suisun | 1930 |
| 5 | Modesto-Turlock* | 1908 | 51 | Alturas* | 1932 |
| | Pajaro Valley* | 1908 | 52 | Dixon | 1931 |
| | Porterville* | 1908 | 53 | Lodi | 1932 |
| 6 | Marysville* | 1909 | 54 | Barstow | 1932 |
| 7 | Woodland* | 1909 | 55 | Contra Costa* | 1933 |
| 8 | Livermore Valley* | 1910 | 56 | Napa | 1933 |
| 9 | Madera* | 1910 | 57 | Pixley | 1935 |
| 10 | Red Bluff* | 1910 | 58 | Delta | 1934 |
| 11 | Fresno* | 1912 | 59 | Santa Cruz | 1935 |
| 12 | Merced* | 1914 | 60 | Visalia | 1934 |
| 13 | Ukiah* | 1914 | 61 | Wasco | 1935 |
| 14 | Healdsburg* | 1915 | 62 | Bakersfield | 1936 |
| 15 | Honey Lake | 1915 | 63 | Kings County | 1937 |
| 16 | Pasadena | 1915 | 64 | Tracy | 1938 |
| 17 | Riverside | 1915 | 65 | Newman | 1938 |
| 18 | San Fernando* | 1915 | 66 | Stocktont | 1939 |
| 19 | Anaheim | 1916 | 67 | Los Banost | 1939 |
| 20 | Los Angeles | 1916 | 68 | Mendota†§ | 1940 |
| $\frac{20}{21}$ | Santa Maria | 1916 | 69 | Sacramento†§ | 1940 |
| 22 | Ventura | 1917 | 70 | Santa Clara†§ | 1941 |
| 23 | | 1918 | 71 | East Side Mesa§† | 1942 |
| $\frac{23}{24}$ | El Centro Grass Valley | 1918 | 72 | Colusa County†§ | 1942 |
| $\frac{24}{25}$ | Willits | 1918 | 73 | Santa Barbara†§ | 1942 |
| $\frac{25}{26}$ | | 1918 | 74 | Coalinga†§ | 1943 |
| $\frac{20}{27}$ | Shasta Valley | 1919 | 75 | Cuyama Valley† | 1943 |
| | Big Valley | 1920 | 76 | Merced† | 1943 |
| $\frac{28}{29}$ | Brawley | 1920 | 77 | Madera [†] | 1949 |
| 29 | Eureka Victorville | 1921 | 1 11 | Maucia | 1930 |

Table 1. Soil surveys in California.

* Out of print; may be consulted in the principal public libraries.

† Not yet published by United States Department of Agriculture.
 § Published by Division of Soils, University of California.

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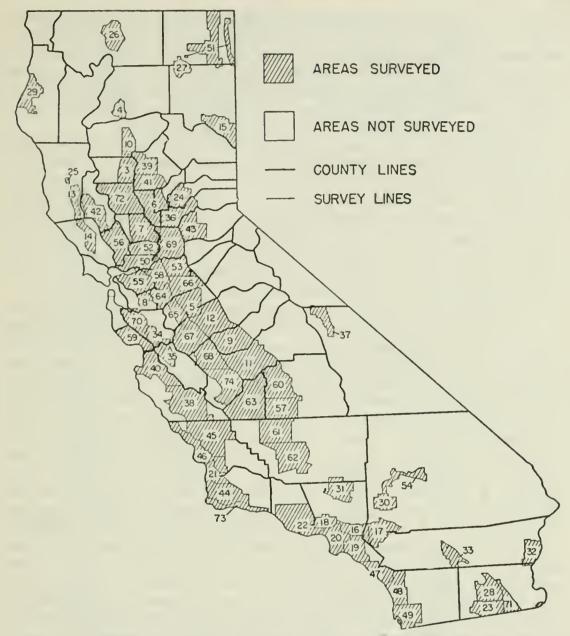


FIGURE 1. Soil-survey areas in California. The numbers refer to the key in table 1

practical and theoretical-problems now being attacked by a well-trained body of scientists.

MAPPING AND CLASSIFYING THE SOILS

Prior to 1913, California showed little interest in a systematic inventory of its soil resources. True, Hilgard was anxious for a soil map based on accurate field surveys; but no legislative support was granted for this purpose. Nevertheless, with the aid of a handcar on the railroad tracks and with horse and buggy Hilgard and his collaborators traveled about the state and prepared a generalized soil map which is now a document of historic interest.¹

During the past 30 years, at first under the leadership of C. F. Shaw, soil survey has flourished and cooperation between state and federal

¹ Perhaps the oldest soil map in the state is that of the San Gabriel Mission, 1857. It shows three types of land, poor, medium, and excellent.

agencies has been very close. Between 1913 and 1918 seven reconnaissance maps were published, eovering some 22,000,000 acres. More than 30,000, 000 acres, slightly less than one-third of the state's area, have been surveyed in detail (scale of published maps, 1 inch = 1 mile). The areas covered by detailed surveys are shown in figure 1 and listed in table 1. There are about 11,000,000 acres of agricultural and potentially agricultural areas for which detailed surveys are still needed.

Soils which have similar profiles and which have developed from a particular type of rock material are grouped together as a series. A series may include two or more soil types differing from one another in the texture of the surface soil. The Yolo series, for example, embraces Yolo sandy loam, Yolo loam, Yolo clay loam, and others. The soil type is the principal unit of mapping and because of its specific character is usually the unit to which agronomic data are definitely related. Sometimes the type is subdivided into phases according to variations in relief, drainage, stoniness, or other factors that affect the agricultural use.

Whenever new areas are surveyed, new series are frequently discovered. Likewise, resurveying of old areas by improved methods leads to a splitting of vaguely defined series into several more accurately defined ones. For example, the Yolo series as mapped in 1915 has since been subdivided into the Yolo, Sorrento, Salinas, and Laguna series. In the earlier days of soil surveying, the series were established mainly on the basis of differentiation of parent material and soil color. Since 1918, nature of subsoil, lime content, reaction (acidity and alkalinity). drainage, and relief have also been taken into consideration. This refinement of soil elassification and survey is reflected in the average areal extent of a soil series, which tends to become smaller. Progress in soil differentiation is accompanied, moreover, by more accurate techniques of mapping. At present, aerial photographs are of much assistance.

The soil map represents a basic inventory that lends itself to a great variety of interpretations. A surprisingly large number of persons and agencies use these maps constantly. County assessors welcome every new map because soil classification serves as a basis for assessment of rural lands. The Constitution of California makes the definite provision that all land of like nature, similarly situated, shall be assessed the same, whether used or unused. With the aid of the soil maps and their modern interpretation, the defense of proper assessment values before boards of equalization and court actions has been greatly simplified. In recent years, federal agencies such as the Agricultural Adjustment Administration, the Bureau of Agricultural Economics, and the Soil Conservation Service have intensified the demand for soil-survey data. Appraisal divisions connected with the Farm Credit Administration and with private banks and mortgage and insurance companies require personnel thoroughly familiar with the interpretation of soil maps. And of course the farm advisor and the seeker after land benefit from detailed and accurate soil surveys.

In figures 2 and 3 a total of 300 soil series have been grouped into 18 broad soil associations to show the general location of the more important California soils. The soils of the uplands and mountains are approximately equal in area to the alluvial soils that occupy most of the valleys and plains. Owing to their agricultural importance, the

| | Present use | | Lumbering, grazing, some irrigated or- chards | Grazing | Grazing, smoother areas farmed | Grazing, smoother, deeper soils dry- farmed to grain | Fimber, grazing, a few areas dry- farmed or in grapes | |
|---|------------------------------|--------------------------|---|---|---|---|--|--|
| cultural use of the soil associations. | General soil characteristics | 84 | 84 | Generally heavy-textured reddish acid soils | Generally heavy-textured stony shallow soils, frequently calcareous in subsoils | Sandy loam soils underlain by bedrock at 2 to 4 feet | Neutral to calcareous soils generally of heavy texture, often shallow | Soils generally acid: variable in depth, texture, and stone content |
| Table 2. Condensed summary of the nature and the agricultural use of the soil associations. | Parent material | Upland Soil Associations | Basic igneous rocks | Lavas, tuffs | Granitic rocks | Sedimentary rocks | Sedimentary and metamorphosed sedimentary rocks | |
| | Important soil series | Uple | Aiken, Auburn, Konokti, Los Posas, Olympic . | Climax, Gleason, Lassen, Underwood | Diamond Springs, Felton, Fallbrook, Holland. Sheridan, Sierra, Siskiyou, Vista | Altamont, Ayar, Caliente, Diablo, Kern, Kettle- man, Linne, Nacimiento, Shedd, Vallecitos, Zaca | Arnold, Carlsbad, Cayucos, Colma, Contra Costa, Goldridge, Ilugo, Kneeland, Los Osos, Mariposa, Moro Cojo, Pentz, San Andreas, Santa Lucia, Sites | |
| | Association | | I. Aiken | 2. Lassen | 3. Holland-Vista | 4. Altamount-Kettle- man | 5. Hugo-Los Osos | |

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| Present use | p Wide range of irri- gated crops | Grazing, dry-land grains | Grazing | oor Grazing, cotton and grain | In Sacramento Valley used for irrigated crops; hay and pasture in places | ac- Wide range of crops | Pasture; very pro- ductive with irri- gation |
|------------------------------|--|--|---|---|---|--|--|
| General soil characteristics | Generally sandy loams, neutral to basic; deep. | Hardpan soils | Gray alkali soils, poorly drained | Dark gray, heavy-textured basin soils; poor drainage | Variable; generally brown neutral to basic | Generally brown soils of neutral to basic reac- tion; deep | Light-colored calcareous soils; deep |
| Parent material | Granitic alluvium | Old alluvium, part granitic, part basic igneous | Granitie alluvium | Mixed alluvium in basin-like areas | Basic igneous allu- vium | Sedimentary allu- vium | Sedimentary allu- vium |
| Important soil series | Cajon, Chino, Chualar, Delhi, Dinuba, Foster, Greenfield, Grangeville, Hanford, Oakdale, Visalia | Alamo, Madera, Redding, Rocklin, San Joaquin, Seville, Yokohl | Domino, Fresno, Lewis, Milham, Pond, Rosa- mond, Traver, Wankena | Merced, Tulare | Bieber, Buntingville, Canby, Delaney, Farwell, Gazelle, Gould, Honcut, Modoc, Nord, Shasta, Stacy, Standish, Surprise, Sutter, Wyman, Vina | Agueda, Botella, Brentwood, Clear Lake, Dan- ville, Dublin, Elder, Esparto, Lockwood, Ojai, Pleasanton, Rincon, Yolo, Zamora | Commatti, Cuyama, Docas, Lost Hills, Panhill, Panoche |
| Association | 6. Hanford-Hesperia | 7. San Joaquin-Red- ding | 8. Fresno-Pond | 9. Merced | 10. Vina-Modoc | 11. Yolo-Sorrento | 12. Panoche-Lost Hills - |

Valley and Terrace Soil Associations

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| Anita, Landlow, Sacramento, Stockton, Willows- Basin deposits of variable origin Burns, Correra, Egbert, Muck, Peat, Roberts, Organic |
|---|
| Carrizo, Gila, Holtville, Imperial, Lareen, Melo- land, Niland, Superstition, Rositas, Woodrow |
| t, Elna, Alluvium of variable Laveen, origin Sunrise, |

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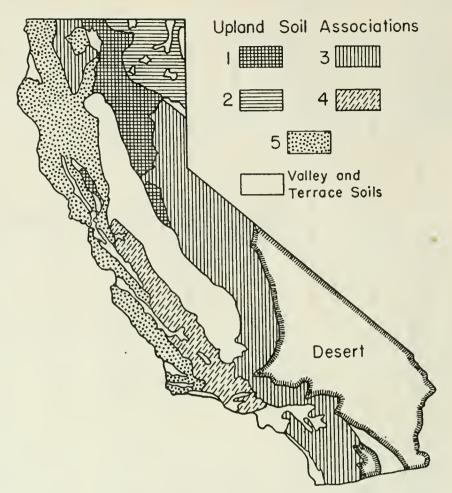


FIGURE 2. Upland soils: 1, Aiken association; 2, Lassen association; 3, Holland-Vista association; 4, Altamont-Kettleman association; 5, Hugo-Los Osos association

valley and terrace soils have been mapped in much greater detail than the others. A condensed summary of the nature and the agricultural use of the soil associations is given in table 2.

For many years, members of the staff of the College of Agriculture have been working on productivity ratings of soils based on soil properties. The Storie Index is a "numerical expression of the degree to which a particular soil represents conditions favorable for plant growth and crop production under good environmental conditions." The index, being restricted to the rating of soils as such, does not include climatic factors that might determine the desirability of growing certain plants in a given location.

The calculation of the index is based on four general factors: A, the character of the soil profile; B, soil texture; C, slope; and X, other modifying factors such as drainage, presence of alkali, degree of fertility, and further miscellaneous conditions. Each of these is evaluated on the basis of 100 per cent for the most favorable or ideal condition, with limiting maximum and minimum ratings ascribed to conditions less favorable for plant growth. A novel feature of the Storie Index, as compared with other scorecard methods, is the principle of multiplication. The numerical values of A, B, C, and X are not added, but multiplied, so that the undesirable and limiting soil characteristics exert a greater influence on the final rating than they would if addition were employed.



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Soil-rating chart (Storie Soil Index rating = factor $\Lambda \times$ factor $B \times$ factor $C \times$ factor X)

| | Factor A Rating on character of physical profil | e | Factor B Rating on basis of surface textur | е |
|-------|---|----------------|---|----------------|
| | | Per cent | | Per cent |
| ŧ. | Soils on recent alluvial fans, flood plains, or other secondary deposits | | Medium-textured : Very fine sandy loam | |
| | having undeveloped profiles | 100 | Fine sandy loam | |
| | x-Shallow phases (on consolidated | | Loam | 100 |
| | material), 2 feet deep | 50- 60 | Silt loam | |
| | x—Shallow phases (on consolidated material), 3 feet deep | 70 | Sandy loam Loamy fine sand | 95 90 |
| | g—Extremely gravelly subsoils | | Silty clay loam | - 90 |
| | s-Stratified elay subsoils | 80- 95 | Clay loam. | 85 |
| II. | Soils on young alluvial fans, flood | | Heavy-textured: | |
| | plains, or other secondary deposits having slightly developed profiles | 95-100 | Silty clay Clay | 60-70 50-60 |
| | x—Shallow phases (on consolidated | 3+7*100 | Light- or coarse-textured; | |
| | material), 2 feet deep | 50- 60 | Coarse sandy loam | 70-90 |
| | x-Shallow phases (on consolidated | =0 | Loamy sand | |
| | material), 3 feet deep g—Extremely gravelly subsoils | 70 80- 95 | Very fine sand Fine sand | |
| | s—Stratified elay subsoils | 80- 95 | Sand | |
| III. | Soils on older alluvial fans, alluvial | | Coarse sand | 30- 60 |
| | plains, or terraces having moderately | | Gravelly: | |
| | developed profiles (moderately dense | | Gravelly fine sandy loam | |
| | subsoils) x—Shallow phases (on consolidated | 80- 95 | Gravelly loam Gravelly silt loam | |
| | material), 2 feet deep | 40- 60 | Gravelly sandy loam | |
| | x—Shallow phases (on consolidated | 10 00 | Gravelly clay loam | |
| | material), 3 feet deep | | Gravelly clay | |
| | g-Extremely gravelly subsoils | 60- 90 | Gravelly sand | 20- 30 |
| IV. | Soils on older plains or terraces having | | Stony: | 70 90 |
| | strongly developed profiles (dense elay subsoils) | 40- 80 | Stony fine sandy loam Stony loam | |
| V. | Soils on older plains or terraces having | 10 00 | Stony silt loam | |
| ۰. | hardpan subsoil layers | | Stony sandy loam | |
| | at less than 1 foot | 5- 20 | Stony elay loam | |
| | at 1 to 2 feet | | Stony clay Stony sand | |
| | at 2 to 3 feet at 3 to 4 feet | | | |
| | at 4 to 6 feet | | | |
| VI. | Soils on older terraces and upland | | | |
| | areas having dense clay subsoils rest- | | | |
| | ing on moderately consolidated or | 40 00 | | |
| **** | consolidated material | 40- 80 | | |
| VII. | Soils on upland areas underlain by hard igneous bedrock | | | |
| | at less than 1 foot | 10- 30 | | |
| | at 1 to 2 feet | | | |
| | at 2 to 3 feet | | | |
| | at 3 to 4 feetat 4 to 6 feet | | | |
| | at more than 6 feet | 100 | | |
| VHII. | Soils on upland areas underlain by | | | |
| | consolidated sedimentary rocks | | | |
| | at less than 1 foot | 10-30 30-50 | | |
| | at 1 to 2 feet at 2 to 3 feet | | | |
| | at 3 to 4 feet | | | |
| | at 4 to 6 feet | 80-100 | | |
| | at more than 6 feet | 100 | | |
| IX. | Soils on upland areas underlain by | | | |
| | softly consolidated material at less than 1 foot | 20- 40 | | |
| | at 1 to 2 feet | | | |
| | at 2 to 3 feet | 60- 80 | | |
| | at 3 to 4 feet | | | |
| | at 4 to 6 feet at more than 6 feet | | | |
| | Conto to a 1000 | 100 | | |

| Soil-rating | chart- | Continued |
|-------------|--------|-----------|
| Nou-runny | Chur e | Continueu |

(Storie Soil Index rating = factor $A \times factor B \times factor C \times factor X$)

| Factor C Rating on basis of slope | | Factor X Rating of conditions other than those in A, B, C | factors |
|---|----------|---|--|
|] | Per cent | | Per cent |
| A-Nearly level (0 to 2 per cent) | 100 | Drainage: | |
| AA—Gently undulating (0 to 2 per cent) | 95-100 | Well-drained Fairly well-drained | 80- 90 |
| B—Gently sloping (3 to 8 per cent) | 95-100 | Moderately waterlogged Badly waterlogged | |
| BB—Undulating (3 to 8 per cent) | 85-100 | Subject to overflow* | variable |
| | | Alkali: | 100 |
| C—Moderately sloping (9 to 15 per cent) | 80- 95 | Alkali-free Slightly affected | $100 \\ 60-95$ |
| CC-Rolling (9 to 15 per cent) | 80- 95 | Moderately affected | |
| D—Strongly sloping (16 to 30 per cent) | 70- 80 | Moderately to strongly affected Strongly affected | |
| DD—Hilly (16 to 30 per cent) | 70-80 | Nutrient (fertility) level: | |
| E—Steep (30 to 45 per cent) | 30- 50 | High Fair | $\begin{array}{c} 100 \\ 95 - 100 \end{array}$ |
| F-Very steep (45 per cent and more) | 5- 30 | Poor Very poor | |
| | 0 00 | Acidity: according to degree | 80- 95 |
| | | | 90- 99 |
| | | Erosion: None to slight | 100 |
| | | Detrimental deposition | |
| | | Moderate sheet erosion | |
| | | Occasional shallow gullies Moderate sheet erosion with shallow | 70-90 |
| | | gullies | 60- 80 |
| | | Deep gnllies | 10- 70 |
| | | Moderate sheet erosion with deep gullies | 10- 60 |
| | | Severe sheet erosion | 50-80 |
| | | Severe sheet erosion with shallow | |
| | | gullies | 40-50 |
| | | Severe sheet erosion with deep gullies- Vcry severe erosion | |
| | | Moderate wind erosion | |
| | | Severe wind erosion | 30- 80 |
| | | Microrelief: | |
| | | Smooth | 100 |
| | | Channels Hogwallows | 60- 95 60- 95 |
| | | Low hummoeks | 80- 95 |
| | | High hummocks | 20- 60 |
| | | Dunes | 10-40 |

The condensed chart of rating criteria shows the values assigned to the various soil features considered in the determination of the index. The method of computation may be made clear by tracing the various steps for a specific soil type. Holland stony loam, for example, has an average depth of 3 feet and is derived from granitic parent material. A considerable number of stones occur throughout the soil mass, and the surface is somewhat gullied. According to the soil-rating chart, the ratings for this soil are as follows:

| Factor | $\mathbf{A}:$ | profile grou | p VII | (depth 3 | feet) | 79 |) per ce | nt |
|--------|---------------|--------------|-------|----------|-------|--------|----------|----|
| Factor | B : | stouy loam | | | | 7 | 0 per ce | nt |

| Factor C: rolling topography | |
|--------------------------------------|--|
| Factor X: occasional shallow | gullies80 per cent |
| Index rating: 70 per cent \times 7 | 70 per cent \times 90 per cent \times 80 per cent = 35 per cent. |

Although still somewhat arbitrary and subjective, the index nevertheless represents a convenient and valuable expression of the quality of California soils as judged by surveyors of wide experience, on the basis of hundreds of thousands of field examinations.

On the basis of index ratings, the soils of California have been classified into six grades, as follows :

Grade 1, index rating 80 to 100: excellent soils, above average in all respects; suitable for a wide range of crops.

Grade 2, index rating 60 to 79: good soils, usually suitable for most crops of the region.

Grade 3, index rating 40 to 59: fair soils, suitable for many crops, but limited in their use because of certain undesirable features (hardpan, drainage, etc.).

Grade 4, index rating 20 to 39: poor soils, suitable for a few crops only.

Grade 5, index rating 10 to 19: very poor soils, extremely limited use, except for poor pastures.

Grade 6, index rating less than 10: non-agricultural areas, such as rough mountainous land, seabland, riverwash, and tidal marsh.

In figure 4 is shown the percentage distribution of excellent (grade 1), good (grade 2), fair (grade 3), and poor (grades 4 to 6) soils in those

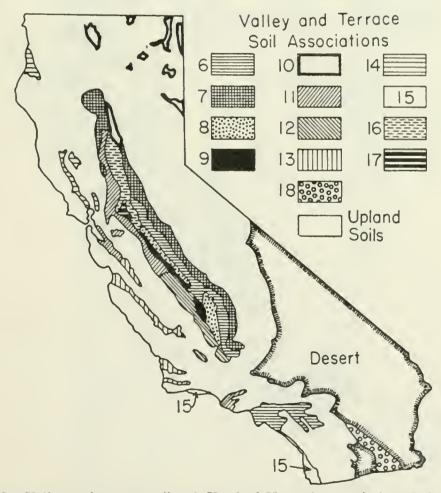


FIGURE 3. Valley and terrace soils: 6, Hanford-Hesperia association; 7, San Joaquin-Redding association; 8, Fresno-Pond association; 9, Merced association; 10, Vina-Modoc association; 11, Volo-Sorrento association; 12, Panoche-Lost Hills association; 13, Salinas-Metz association; 14, Ferndale-Bale association; 15, McClusky-Olivenhain association; 16, Stockton-Sacramento association; 17, Ryde-Roberts peat-muck association; 18, Imperial-Coachella association

| profiles |
|------------|
| soil |
| California |
| Typical |

| | œ | "Alkali" soil | Lahontan loam | Alkali-indicating sgetation | Low rainfall |
|--------------------------|--|---|-------------------------------|--------------------------------|-----------------|
| | | | Lal | Alkali-in vegetation | Lov |
| 8 | 2 | "Red desert" soil containing line concretions | Superstition sand | Desert shrubs | Low rainfall |
| Valley and terrace soils | 9 | Marine terrace soil with claypan | Olivenhain loamy fine sand | Shrub | Medium rainfall |
| A. | Q4 | "Hydromorphie" basin soil | Clear Lake adobe clay | Water-loving grass | Medium rainfall |
| 4 | Alluvial fan soil | Yolo loam | Tree and grass cover | Medium rainfall | |
| Upland soils 2 3 | "Gray brown forest" soil devel- oped on shale rock | IIugo loam | Tree cover | High rainfall | |
| | "Prairie" soil de- veloped on soft sandstone | Colma loam | Grass cover | Medium to high rainfall | |
| | 1 B | "Lateritic" soil de- veloped on basic igneous rocks | Aiken elay loam | Tree cover | High rainfall |

^a Numbered columns refer to soil profiles shown in plate I.

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areas in California for which detailed soil surveys are available. As may be seen, in some areas of the state excellent and good soils predominate, whereas in others inferior soils make up the largest proportion. The following acreages for all areas surveyed have been computed:

| Grade 1, excellent soils_ | 3,457,613 acres |
|---------------------------|------------------|
| Grade 2, good soils | 3,194,766 acres |
| Grade 3, fair soils | 5,160,369 acres |
| Grades 4 to 6, poor soils | 12,905,890 acres |

Figure 5 shows the exact location of the most valuable soils in the state. The soils of superior quality tend to be found in the valleys.

It is often difficult for the layman to grasp the full significance of the soil inventory that is contained in the soil-survey reports and maps. In recent years natural land divisions have provided a simple key to

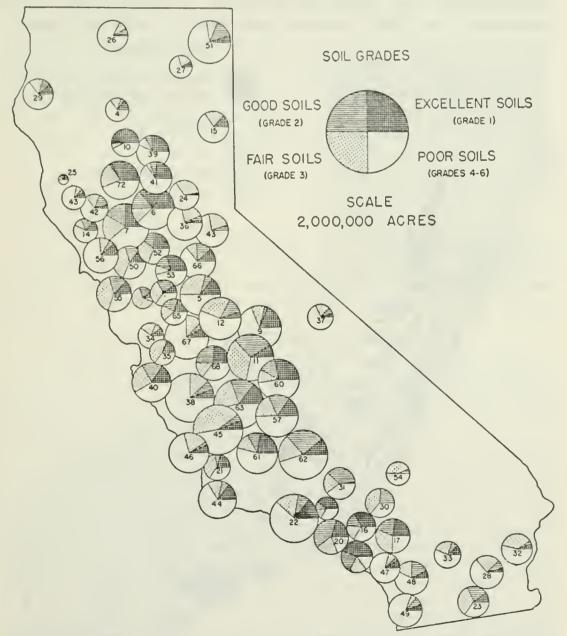


FIGURE 4. Distribution of soil grades in soil-survey areas. The relative area in each survey is indicated by the size of the circle in relation to the scale in the legend (which is not in true proportion to the area of the state as a whole). The numbers in the circles refer to the key of the soil surveys given in table 1

the interpretation of soil-survey knowledge. They are arrangements of soils according to topography, slope, texture, profile development, drainage, alkali content, erosion, nutrient level, and micro-relief. The first four properties are permanent factors, the other five more or less changeable by man. All soils that are similar in these particulars constitute a natural land division and are designated by a symbol consisting of letters and numbers. The scheme of symbols is too complex to be presented here in detail. It may suffice to give a few specific illustrations and, at the same time, point out the relations to crop production. The Lodi area (fig. 6) is chosen for this comparison.

Land Divisions $A_1 - A_4$ (Orchards, Grapes). The letter A indicates alluvial fans or flood plains with smooth topography. The subscripts denote textural characteristics of the surface and subsoils. Thus, A_1 is a medium-textured soil (loam) having a deep permeable subsoil. A_4 is a fine-textured soil (clay) having a moderately dense subsoil. A_2 and A_3

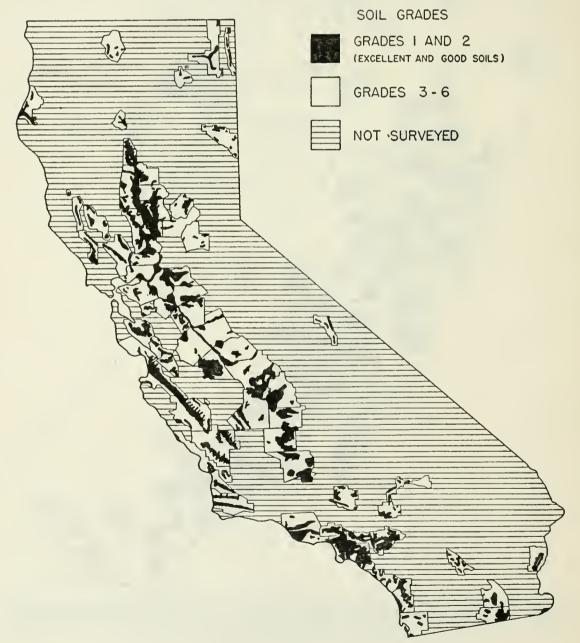


FIGURE 5. Location of excellent and good soils in California

have intermediate textures. Most A soils are excellent or good (index 60 to 100). In the Lodi area, as well as through the interior valleys, these soils are characterized by a preponderance of exacting and deep-rooted crops such as walnuts, peaches, cherries, plums, table grapes, and juice grapes. As seen from figure 6, a considerable area of orchards and grapes extends northward into another group of soils that is less productive. Here the yields are much lower than in A-type land.

Land Division $B_1 - I_p$ (Truck Crops and Corn). The letter B denotes smooth basin lands, and the subscript indicates medium texture. The symbol I_p expresses poor drainage conditions. These soils have an index rating of 60 to 80. As indicated in figure 6, asparagus, potatoes, sugar beets, and corn are grown almost exclusively on this group of soils. In general, the area of this natural land division $B_1 - I_p$ coincides with the distribution of irrigated truck and field erops.

Land Division C_1 , D_1 , E_1 (Dry Pasture). The letter C represents lower terrace land, which is generally smooth and normally occurs along the edge of valleys; D represents terrace land, smooth to rolling; E represents upland, which is in general hilly, or rolling to steep. The rating of the soils of these land divisions varies with texture, nature of the subsoil (hardpans, claypans), slope, stone content, and erosion. As a rule, dry pastures of good grass quality characterize these areas. The C group also includes sizable areas of non-irrigated grain and hay.

Land Division M (Moist Pastures). The area labeled "M" contains a moderate amount of alkali. Moist pastures with alkali-tolerant grasses are the predominating crop.

Each land division consists of numerous soil types, which determine the local practices of soil management. Thus, without sacrificing the intrinsic values contained in the detailed soil surveys, the reclassification of the individual soil types into natural land divisions greatly facilitates the broader agricultural analysis of the intricate soil pattern of a given region.

SOME WHY'S AND WHAT'S OF CALIFORNIA SOILS

The scientist wants to know why California soils are as they are. In contrast to the practical agricultural schemes of soil classification, the scientific systems represent arrangements of soils according to their origin and mode of formation. This sort of study throws light on soil genesis and permits a world-wide comparison of soils.

For many decades the soils of California seemingly did not fit into the prevailing scientific systems of soil classification. As late as 1935, Marbut in his *Soils of the United States* was unable to delineate in California representatives of the great climatic soil groups of the world. But the gap is now being bridged. Advancements in the viewpoints on soilforming processes and soil classification, and a reemphasis on the laboratory studies of California soils by the University, promise a rejuvenation of the classical period of Hilgard. It has been tentatively established that many representatives of the major zonal and intrazonal soils of the world, such as prairie soils, podzols, chernozems, arid brown soils, lateritic soils, rendzinas, solonetz, solonehak, and gray-brown podzolie soils, occur in California. There are strong indications that a fresh attack on problems of soil formation in the state will contribute greatly to the advancement of a truly scientific classification of soils. Perhaps the most important contribution of the scientific study of soils is the dynamic interpretation of the *soil profile*. Instead of considering soils as a mere mass of inorganic and organic material, soil scientists emphasize certain elements of organization that are found in every soil. In their natural state, soils exhibit characteristic strata, or horizons,

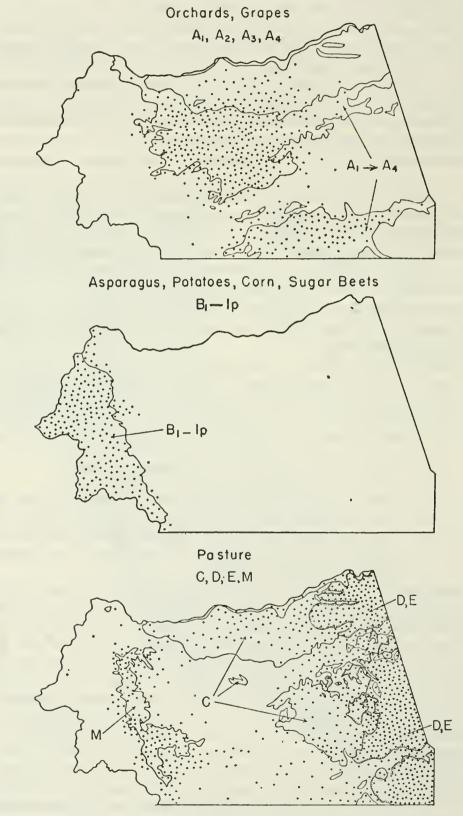


FIGURE 6. Relations between natural land divisions and distribution of crops in the Lodi area. Each dot represents 100 acres



.1, ALKALI SOIL BEFORE RECLAMATION



B, ALKALI SOIL AFTER RECLAMATION



LAYOUT OF EVAPORATION AND TRANSPIRATION EXPERIMENTS

which are the result of processe of our or reation upper the influence of chicar - and coretation. Bloadly specking these for zons are classified as A horizons and B horizons, which outcoshould is some reasure to the layman's of a of surface soils and sub-oils. Chica tenstic profiles of representative Cautomics of a reashey non-plate 1.

A conspicuous f ature in the evolution of soils is the participation of organic life. Sold not only provides a livelinor d for plants, but is also a storehouse for an inmense variety of small organisms and microorganisms, especially bacteria. Without their activities, their docomposition, and their synthesis of organic substances, the soil would not be the deheately balanced dynamic system that it is, but an inert pile of weathered rock debris.

The dynamic relations of a soil are conditioned mainly by elimate, organisms (vegetation), topography, parant material, and time. In California, because of the sharp contrasts in climate and vegetation and because of the complexity of geologic formations, unique opportunities are offered for evaluating the role of soil forming factors. Although detailed investigations are still lacking, certain broad features clearly stand out. Thus, Hilgard and later R. H. Loughridge showed that the average humus content of surface soils was lowest in the desert plains 10.51 per cent, and, with the exception of tules and meadows, highest in the Coast Range valleys [1.69 per cent]. The San Joaquin Valley [0.79] per cent and the Sacramento Valley 1.14 per cent had intermediate values. Loughridge attributed the high humus content of the Coast Range valleys to the greater humidity of that region and a denser vegetation. Shaw also noted that in California the soils of the desert areas are distinctly lighter in color and lower in amount of organic matter than those of the more humid areas.



An illustration of the dependence of soil features ² on climate is supplied by a study of soil acidity and soil alkalinity. In California, soil reaction varies within wide limits. Podzol-like soils along the Mendocino Coast are extremely acid (pH 4.3), whereas some of the alkali soils of the San Joaquin Valley and the desert regions are strongly alkaline (pH above 10). Most agricultural soils of the state have nearly neutral reaction (pH 6.8 to 7.2). Comparison of the soil-reaction map (fig. 7) and the precipitation map (fig. 8) shows that acid soils predominate in regions having high precipitation, and basic soils in regions having low precipitation. The degrees of acidity or alkalinity are influenced also by the parent material, the topographic features, and the age of the soil. The dependency on parent material is particularly evident in regions of intermediate rainfall, where calcareous rocks tend to produce soils having alkaline or neutral reaction, while standstones low in bases give rise to neutral and acid soils.

The distribution of lime in the soil (fig. 9) also reflects in part the direct and indirect influences of climate. The extensive black areas which denote soils having lime (calcium and some magnesium carbonate) in all parts of the profile are mostly in regions of low rainfall. The converse relation, however, does not necessarily hold. That is, some soils, especially those derived from rocks low in calcium content, may have no free lime, even under conditions of low rainfall. In regions of intermediate rainfall, most of the soils are free from lime in the surface but have some in the subsoil. In regions of high rainfall, mature soils contain little or none.

The nature of soil reaction and the presence or absence of lime in the soil have a direct bearing on soil-management practices. These more utilitarian aspects will be considered in the section on fertilizers and nutrition of plants.

In the older and more mature soils of California the existence of pronounced B horizons, or subsoils, is very common. Soil surveyors distinguish between clayplans, iron hardpans, and lime hardpans. The claypans are characterized by horizons of high clay concentrations, from 5 to 20 inches in thickness, that hamper water penetration and root development. Such soils are restricted to the growth of grasses, grains, and shallow-rooted field crops. Orehards do not make satisfactory growth on them.

In Santa Cruz County, apple production on old soils having dense elay subsoils was about 140 boxes per acre per year (1934-1936); on soils having moderately dense subsoils it was about 380 boxes; and on deep, friable, alluvial soils, nearly 1,000 boxes.

As may be noted from figure 10, claypan soils are widely scattered over the state. Striking examples are found on marine terraces throughout the Coast Range and in the Great Valley. In 1949, 60 soil series were known to have elaypans.

Iron hardpans and lime hardpans are horizons in which the sand and silt grains are elemented together with iron hydroxide and silica gels or with lime. These strata, which may approach the hardness of concrete pavement, vary in thickness from a few inches to more than a foot. Paradoxically, many productive eitrus, fig, and olive orehards are found on some of the iron-hardpan soils. Their growth is facilitated by holes blasted through the hardpan before the trees were planted. The agricultural value of hardpan land is in direct proportion to the depth of

² A detailed soil reaction map in colors is contained in California Agr. Exper. Sta. Bull. 712, 1949.

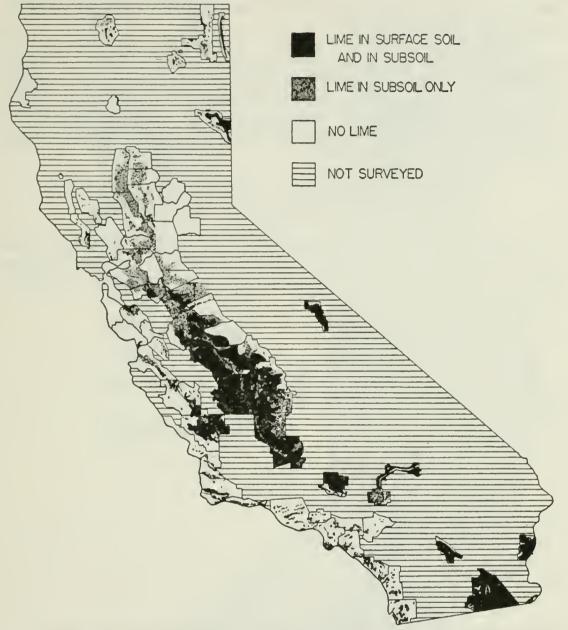


FIGURE 9. Distribution of lime (calcium carbonate) in California soils

the soil above the hardpan (see soil-rating chart, soil-profile group IV). For example, in certain parts of Fresno County, hardpan occurs at a depth of 10 feet or more and, accordingly, the soil rating is relatively high. According to figure 10, the iron and lime hardpans occur most abundantly on the eastern part of the Sacramento and San Joaquin valleys, where they occupy the elevated ridges and the mesas of old alluvial fans. The hardpan soils comprise twenty-four soil series.

One of the important characteristics of a soil is its *texture*. With the aid of mechanical analysis the mineral portion of the soil may be separated into particles of various sizes, ranging from sand grains (0.1-1.0 millimeter in diameter) to clay particles (less than 0.005 millimeter in diameter). The finest fraction of the clays is known as colloidal clay. The various proportions of the mineral particles determine the texture of the soil. According to the preponderance of a specific particle group, soil scientists distinguish between sands, silts (medium-sized particles), and clays. Loams contain 30 to 50 per cent sand, 30 to 50 per cent silt, and less than 20 per cent clay.

Owing to the important effect of texture on many physical and chemical features of the soil, such as the storage eapaeity for water, permeability, tilth, and nutrient content, two maps have been prepared that permit a survey of the textural variations of California soils. Figure 11 gives the proportions of sandy soils, loams, elay loams, and elay soils in specific soil-survey areas. This grouping comprises the following detained texture classifications:

> Sands: sands, fine sands, and loamy sands Loams: sandy loams, fine sandy loams, silt loams, and loams Clay loams: silty clay loams and clay loams Clays: silty clays, clays, and adobe clays

In some survey areas sands are the most abundant; in others the clays predominate. In preparing figure 12 an attempt was made to bring out the dependence of texture on physiographic features. Naturally,

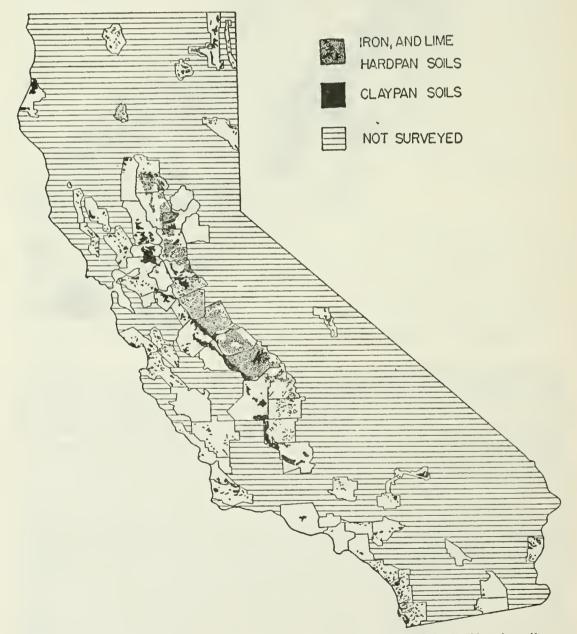


FIGURE 10. Occurrence of characteristic B horizons (subsoils) in California soils

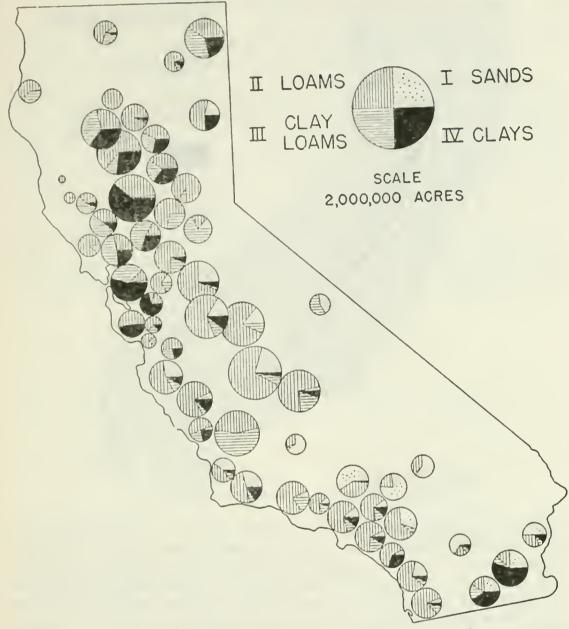
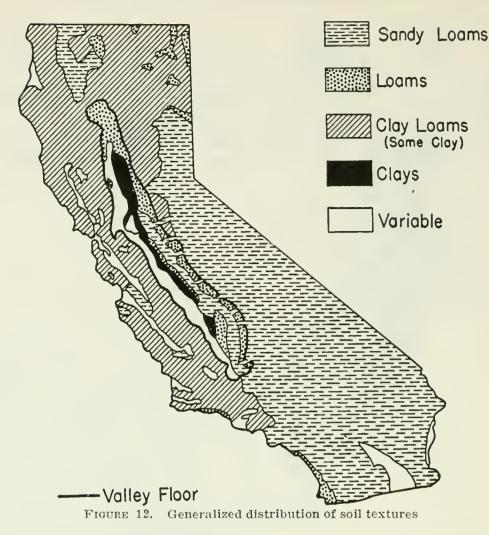


FIGURE 11. Proportions of sands, loams, clay loams, and clays in soil-survey areas

in order to focus attention on the broader aspects, many local conditions had to be omitted and, outside of detailed survey areas, estimations had to be made.

According to figure 12, three major texture provinces may be differentiated in the state. First is the region of eoarse-textured soils (sandy loams) which comprises the Sierra, the deserts, and the major part of the state south of Los Angeles. These soils are derived, to a large extent, from acid igneous rocks. The relatively low clay content may be attributed partly to climate; for, as is shown elsewhere, low rainfall accompanied by high temperature, as in California deserts, tends to retard clay formation. A similar retardation of weathering seems to be produced by the combination of high rainfall and low temperature that is typical of the Sierra. The second texture province, consisting of clay loams, embraces much of the Coast Range and a large part of the northeastern mountain area. In the Coast Range the fine texture is probably due to the prevalence of shales and sandstones rich in clay. In Modoc,



Lassen, and Shasta Counties, basic igneous rocks are widely distributed. These weather readily and, in general, produce much elay. The third texture province may be assigned to the Great Valley, which abounds in variability and complexity of textures, yet in some degree reflects the textures of the soils of the surrounding higher elevations. While a broad strip along the eastern part of the Valley is occupied by loam, the trough is rich in clay. These fine-textured alluvial soils are the result of transportation and slow sedimentation of soil debris from the mountains.

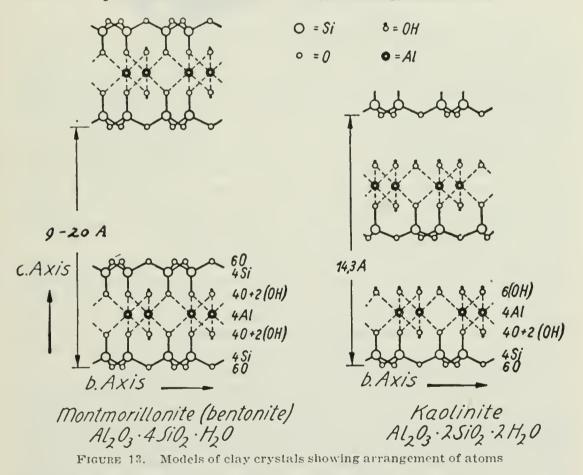
SOLVING THE MYSTERY OF CLAYS

A few years ago California scientists examined soil clays with the aid of X-rays and discovered that, contrary to prevailing teaching, clays are definitely crystalline. Crystallinity implies that the atoms within a clay particle are not distributed at random, but are oriented according to a definite plan or pattern. The discovery of the crystallinity of clay, made independently and simultaneously in other parts of the world, stimulated intensive research, which greatly clarified the nature and behavior of colloidal clay particles. According to most recent information, the groups of clay minerals that occur abundantly in California soils are montmorillonitic clays, illite, and kaolinitic clays.

Montmorillonitic clays have expanding lattices and exhibit pronounced swelling and shrinking. They have a base-exchange capacity of about 100 milliequivalents per 100 grams of clay. A high proportion of these clays is found in the Ducor, Farwell, Herdlyn, Holtville, Imperial, Maxwell, Porterville, Rincon, Sacramento, Sorrento, Stockton, and Yolo soil series. The characteristic adobe structure of many California soils is caused by the elay of this type.

The crystal lattice of illite is related to that of montmorillonite, on the one hand, and to those of the common mica minerals, on the other. It does not swell and has a considerably lower base-exchange capacity than montmorillonite. It seems to dominate in the Antioch, Canby, Fresno, Hanford, Huerhuero, Placentia, Ramona, Rosamond, San Joaquin, and Waukena soil series. The strong fixation of potassium fertilizers which occurs in some of these soils may be conditioned in part by illite, but this has not yet been proved.

Kaolinitic clays are found in a large number of soils. They do not swell in water and their base-exchange capacity is even lower than that of illite, usually less than 25 milliequivalents per 100 grams of elay. They may fix large amounts of phosphates. Kaolinite and its relatives were found in representatives of the Aiken, Corning, Fallbrook, Holland,



Keefers, Madera, Redding, Sierra, and Siskiyou soil series, and in some degree in the Saeramento and the San Joaquin series.

The impact of these new concepts on agricultural soil research is bound to be far-reaching. Crystal chemistry of clays has opened new roads toward a successful solution of many age-old problems in soil chemistry and soil physics. Substantial gains in the knowledge of colloidal behavior have resulted from the use of such modern tools of science as the ultramicroscope, the polarizing microscope, the electron microscope, X-ray equipment, and radioactive indicators. Many nonagricultural uses of clays, as in pottery and ceramics, in oil drilling, in constructing the foundations of buildings, and in making highways, have been placed on a more secure basis by these investigations.

A number of significant characteristics of the soil that influence its productivity are conditioned by the architectural arrangement of the soil particles, which is commonly designated *soil structure*. The arrangement and orientation of the clay particles in the soil can be altered within wide limits through methods of soil management, and such alterations are of consequence to agriculture.

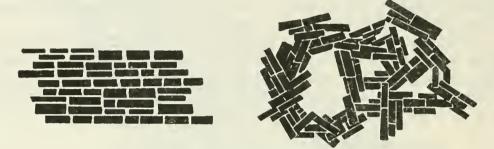


FIGURE 14. Schematic arrangement of a dispersed soil (left) and a flocculated soil (right), after drying

In structure, soils may be either dispersed or flocculated. The nature of the two structures is shown diagrammatically, according to present knowledge, in figure 14. The little rectangles represent side views of the elay particles, which are known to possess the properties of thin platelets. In a dispersed soil, when dried, these platelets appear to be arranged in a very orderly fashion. Every particle is snugly surrounded by other particles, and consequently the spaces between the particles are small and the intercommunicating channels are exceedingly narrow. Water and air permeate such a soil very slowly. In the sun, it bakes to a condition of extreme hardness. Plant growth is adversely affected.

In contrast, a flocculated soil has an open, loosely packed structure. Although the minute clay plates may show orientation within small clay clusters, or aggregates, the essential feature is the open network of the aggregates. This architectural pattern favors relatively large intercommunicating channels and permits easy circulation of water and air. Such soils are said to have a good structure; in fact, this open-packed crumb structure is an essential characteristic of a productive soil.

Excessive cultivation and certain degrees of alkalization tend to produce dispersed (puddled) soils, while incorporations of organic matter and sometimes of such salts as gypsum and lime tend to maintain soils in a floceulated state. In a laboratory experiment, before drying, the entire contents of a pan of elay soil was a muddy mass. During drying, the dispersed elay particles arranged themselves in close packing, and, in consequence, dense, hard clods developed, separated by large eracks. This arrangement is known as adobe structure. Ground alfalfa was incorporated and the moist mixture was left undisturbed for four months, during which time active decomposition took place. Then the soil was dried, and an open, friable crumb structure resulted.

Rewetting of adobe soils produces swelling and results in the formation of an impervious plastic mud. Rewetting a flocculated soil does not change significantly the favorable erumb structure.

FIGHTING SOIL ALKALI

The University of California in 1874 called Professor Hilgard to lead the agricultural work of the young institution. Here was a man with vision who possessed a profound knowledge of the fundamental sciences of chemistry, geology, and botany, and who was enthusiastic and eager to apply this knowledge in the service of agriculture. Hilgard is recognized throughout the civilized world as one of the founders of soil science. In California his name is inextricably associated with the problem of alkali soils, since he laid the foundation for much of what is known today about their nature, origin, and reclamation.

In California more than 4,500,000 acres of alkali soils have been mapped in detail. They consist of about 1,333,000 acres of strong alkali and about 3,125,000 acres of moderate and slight alkali. The determination of the alkali content of soils is based on conductivity measurements, and the results are expressed in terms of air-dry soil as follows:

Alkali-free: less than 0.20 per cent alkali Slight alkali: 0.20-0.39 per cent alkali Moderate alkali: 0.40-0.99 per cent alkali Strong alkali: 1.00 or more per cent alkali

Multiplication of these figures by 10,000 converts the percentage values into parts per million (p.p.m.), a mode of expression frequently used in agricultural literature. The alkali usually consists of combinations of the following:

> Sodium (Na+) Potassium (K+) Magnesium (Mg++) Calcium (Ca++) Chloride (Cl-)

Nitrate (NO₃⁺) Bicarbonate (HCO₃⁺) Carbonate (CO₃⁺) Sulfate (SO₄[±])

These combine to form various salts, such as sodium bicarbonate, calcium chloride, and magnesium sulfate.

It is not yet possible to predict accurately the effect of the amount and the composition of the salts on plant growth. Many years ago, Hilgard stated that the upper limit of plant tolerance for alkali salts varies somewhat as follows:

> Sodium carbonate : 0.10-0.25 per cent Sodium chloride : 0.20-0.50 per cent Sodium sulfate : 0.50-1.00 per cent

Experience, however, has shown that much smaller amounts may be very injurious to some plants, and larger amounts may cause little trouble to others. Greenhouse experiments further indicate that there are no specific critical salt concentrations. Rather, there is a gradual decrease in growth as the salt concentration becomes higher. Much depends on the location of the alkali in the soil, whether mostly near the top or uniformly distributed through the zone of plant roots. The general fertility level also is of importance. It has been asserted that a liberal use of barnyard manure may permit production of a good crop on soil containing so much salt that without the fertilizer little could be grown. Yet this observation cannot be generalized. The moisture content of the soil is another significant factor. As the soil dries out, through transpiration and evaporation of water, salt becomes more concentrated in the remaining solution and alkali injury ensues. Climate is still another factor. A given salt concentration is more harmful in the hot and dry portions of the central valley than in the cool and humid areas of the coast. Last but not least, the kind of plant itself has to be taken into consideration. Sugar beets, Bermuda grass, rice, and cotton are much more tolerant than eitrus, walnuts, beans, and melons. To obtain accurate information about relations of alkali and plants, the University and the United States Bureau of Plant Industry, Soils, and Agricultural Engineering are conducting numerous and accurately controlled experiments with plants grown in nutrient solutions and in alkali soils.

In 1924 and succeeding years, boron injury was discovered in the state. Since then, much attention has been directed to the boron content of soils and irrigation waters. Small amounts of boron appear to be necessary for the satisfactory growth of most plants, but toxic

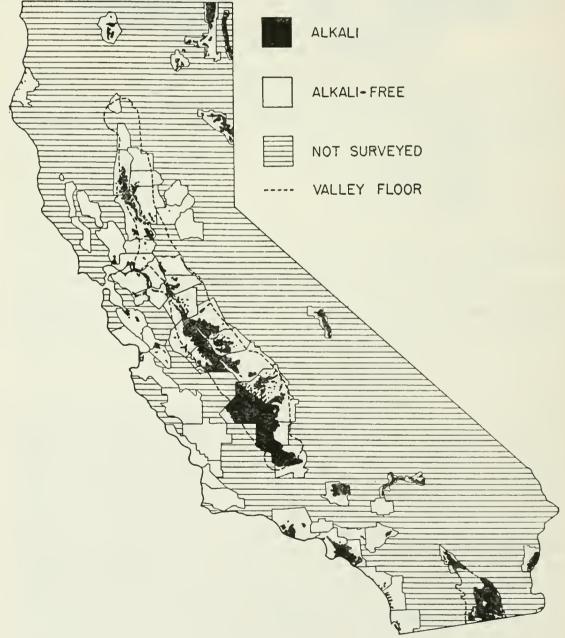


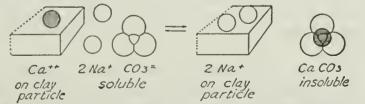
FIGURE 15. Distribution of soils containing alkali

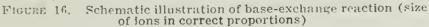
concentrations are readily reached. In soil solutions, concentrations of boron that are insufficient to support normal plant growth are usually below 0.1 to 0.5 p.p.m. If the boron content of irrigation water is in excess of 1.0 p.p.m. (0.0001 per cent), injury to sensitive plants, such as the lemon, grapefruit, avocado, orange, and apricot, may be expected.

The distribution of alkali soils is shown in figure 15. In interpreting this map several limitations must be kept in mind. First, the black areas include all kinds and all degrees of alkali. The most extensive areas (more than 50,000 aeres) of strong alkali occur in the Alturas, Kings, Bakersfield, Waseo, Los Banos, Merced, and Brawley soil-survey areas. The map does not distinguish between white-alkali and black-alkali soils. The former contain an excess of neutral salts, usually chlorides and sulfates. The latter contain injurious amounts of soluble carbonates, with or without chlorides or sulfates. Second, the distribution of alkali is often very spotty. Variations ranging from no alkali or slight alkali to strong alkali may occur within a few square rods. Third, the presence of some alkali in the soil by no means excludes agricultural use of the land. As a matter of fact, comparison of the alkali map with the soilrating map (fig. 5) shows that some of the alkali soils even qualify as excellent or good soils (compare also the soil-rating chart, factor C). In spite of these limitations, the alkali map has intrinsic value because the presence of alkali, even in small amounts, necessitates more careful soil-management practices.

The formation of alkali soils is usually conditioned by dry elimates and high water tables. The ground water of arid regions, in contrast to that of humid regions, is commonly rich in dissolved salts. If the ground-water table is near the surface, say within 5 or 10 feet, water tends to rise by capillarity and to evaporate, leaving the dissolved salts in the soil. In other words, the soil acts like a wick. Owing to the high rate of evaporation and the low precipitation in arid regions, large amounts of soluble salts may thus accumulate in the upper part of the soil.

Occurrence of a high ground-water table depends on a number of factors, geologic as well as man-induced. For example, there are thousands of acres of farm land in California which were formerly highly productive, covered with valuable orchards and vineyards, but which later became severely injured by alkali brought up by eapillarity from a high water table that developed as a result of seepage from canals and excessive irrigation. This destructive phenomenon is equally well known in other irrigation regions of the world and is popularly known as the rise of the alkali.





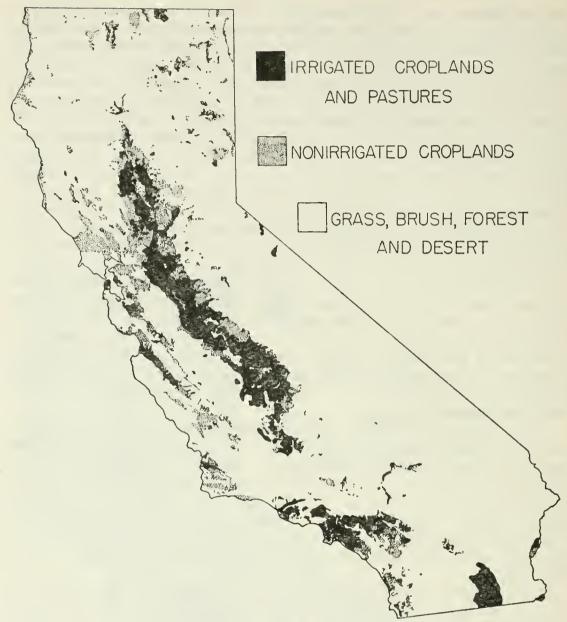


FIGURE 17. Distribution of irrigated croptands and pastures

Continued application of saline irrigation water, also, may cause serious injury to the soil if the salts in the water contain a high proportion of sodium compounds, particularly sodium carbonate or bicarbonate.

It was formerly believed that the ill effects of alkali soils were entirely attributable to the toxic effects produced by high salt concentrations. Now, we know that the salinization of a soil initiates a great number of chemical and physical changes that indirectly affect its productive power.

Sodium salts may react chemically with the clay and humus colloids of the soil, the interreaction being known as a "base exchange" or "exchange adsorption." If sodium carbonate is added to a soil containing exchangeable calcium, the sodium ions displace the calcium ions from the surface of the clay particles and stick there even after removal of free salts. The transformation from a calcium to a sodium clay is accompanied by very pronounced changes in the physical make-up of the soil. Sodium clays tend to be dispersed and, as in other dispersed soils, the clay particles, upon drying, may arrange themselves in a closely packed mass that is destructive to the productivity of the soil. The pore space of the soil may be so much reduced that water percolation is nil and plant growth becomes adversely affected. This change in soil structure, which has been overlooked in the past, supplies the key to any successful reclamation.

Assuming a causal connection between the decline of ancient irrigation civilizations and the rise of alkali, some authorities have advanced the opinion that the permanence of irrigated agriculture is doubtful. There is good reason for believing, however, that with the aid of the present knowledge of alkali soils, together with anticipated future scientific developments in the fields of soil chemistry, soil physics, and plant nutrition, crop production on irrigated soils can be maintained for fully as long a time as on the non-irrigated soils in humid climates

Already, distinct successes have been achieved in solving the problem of reclamation of alkali soils having relatively coarse textures. In this undertaking two basic tasks must be kept in mind: first, removal of excess salt; and second, maintenance of a good soil structure. The first step to be taken is the establishment of good drainage conditions. The importance of favorable drainage conditions can scarcely be overemphasized, for water is the only agent by which soluble salts can be removed from the soil in a practical way.

The second step with black-alkali soils is the conversion of sodium elay to calcium elay. This may be accomplished or aided by adding to the soil such chemicals as gypsum, sulfur, iron sulfate, and alum. Extensive investigations at Fresno have demonstrated that, among the materials just mentioned, sulfur (1,000 pounds per acre) was the most economical. Marked improvement was obtained by the reelamation of a black-alkali soil on the Kearney Vineyard experiment field near Fresno (see plate 2). In 1920, when reelamation was begun, barley, harvested as hay, yielded only 616 pounds per acre. Addition of gypsum and plowing under of melilotus, accompanied by heavy irrigation to leach out the salts, subsequently encouraged the growth of alfalfa, which in 1928 yielded nearly 10 tons per acre. The land still produces large yields of alfalfa. The poor physical condition of the original alkali soil, characterized by harsh clods, has disappeared and the soil is now mellow and granular.

Recent investigations have, however, indicated that by using soil permeability as an index, a spacing and depth of drain may be determined for this area which will not only successfully but economically control the water table in the medium and light textured soils of this area. The lowering of the water table must be accompanied by leaching to remove the excess soils from the surface soils.

Many white-alkali soils contain sufficient amounts of calcium salts to bring about the formation of calcium clay after leaching. No ameliorants need be added to these soils. In certain parts of the Imperial Valley, large yields of crops have been produced by the simple expedient of drainage and leaching without applying any chemical treatment whatever.

WATER IN SOILS, CALIFORNIA'S PARAMOUNT PROBLEM *

With respect to agricultural production, California's climate has two unusual characteristics. First, there is a wide range in the total annual precipitation, varying from almost none to more than 100 inches; and second, there exists a very unequal seasonal distribution of rainfall, characterized by wet winters and dry summers. In the zones of high and medium winter rainfall, enough moisture is usually stored in the soil to carry crops to June 1, but thereafter water must be supplied by artificial means. Extensive and costly irrigation systems are the arteries of California's great agricultural development. Yet, in the last analysis, the economic feasibility of the entire irrigation enterprise rests on the producing power of the soils that are irrigated.

California's land area comprises about 100,000,000 acres. The agriculturally valuable land may be classified as follows:

| Grazing land † | 25,200,000 acres |
|---|------------------|
| Crop land, dry-farmed | 4,900,000 acres |
| Crop land, irrigated | 3,500,000 acres |
| Pasture, irrigated | 1,200,000 acres |
| Miscellaneous farm lands | 1,500,000 acres |
| † Grass, woodland grass, and sagebrush in Great Basin area used f | or grazing. |

The total area irrigated amounts to about 5,000,000 acres. Its distribution is shown in figure 17. In spite of the relatively small acreage of the irrigated land, the economic returns from it constitute a very large share (83 per cent) of the total received from agriculture for all productive lands of the state: in 1940 the value of all crops was \$537,-000,000, whereas the value of the irrigated crops alone was \$446,000,000. The proportions of the various types of crops on the irrigated lands as of 1929 are as follows:

| Crop | Acres | Crop | Aeres |
|----------------------|---------|-------------------|---------|
| Alfalfa | 719,600 | Cotton | |
| Small grains and hay | 623,100 | Subtropical fruit | 251,100 |
| Small row crops | 562,400 | Large grains | 118,100 |
| Deciduous fruits | 527,400 | Rice | S0,700 |
| Grapes | | Miscellaneous | 900 |

Irrigation in California was begun at the Franciscan missions and Spanish pueblos of Los Angeles, San Jose, and Branciforte. It was practiced to a limited extent on a few of the private ranches during the mission period and more extensively as American and other "foreign" settlers acquired farms or ranches in the 'forties and 'fifties. More rapid expansion of irrigation began in the 'sixties and 'seventics, reaching its highest rate in the two decades between 1900 and 1920. Even as early as the 'fifties and 'sixties, in some parts of the state, corporate and community construction of irrigation works was undertaken. Now, with the decline in the number and importance of corporate, or ''commercial,'' irrigation enterprises, irrigation or other types of districts, and mutual water companies, have become the dominant types of irrigation organizations, and private pumping plants the principal means of supplying

^{*} No attempt is made here to deal comprehensively with irrigation in California. Except for general statements regarding the nature of the state's water problem and how it is being dealt with, the discussion presented stresses some of the technical phases of soil, water, and plant relations, and irrigation waters. For further information the reader is referred to the many university, state, and federal reports and bulletins dealing with the various aspects of this subject.

water by individual enterprise. In recent years the United States Bureau of Reelamation has become a material factor in supplying water to California farmers through its construction of the All-American Canal in the Imperial Valley and the development of the Central Valley Project, now under way.

California's problem of water supply lies in the distorted relation between agricultural demand and natural water supply. In figure 18 the state has been divided into seven water-resource basins. The bars and corresponding percentage figures indicate the proportions of the agricultural lands and of the available water resources within each basin.

The discrepancy between supply and demand is most important in the San Joaquin Valley and in the southern California coastal plain. The general situation with reference to the water resources was pointed out in a federal report issued as early as 1873, and in reports of the State Engineer issued in the 'eighties. Thirty years ago, in a report prepared for the State Conservation Commission, cooperating federal, state, and university workers mapped the irrigable and irrigated lands of California and summarized the water resources of the state on the basis of the information then available. This and the previous studies showed a large surplus of water over needs in the Sacramento Valley and serious deficiencies in the San Joaquin Valley and in the southern coastal plain. The extensive investigations of the State Division of Water Resources and numerous federal agencies during the past twenty years have still further emphasized this situation. They have also pointed out means for its alleviation where this appears to be feasible.

Their solution for the San Joaquin Valley is the Central Valley Project, which aims at preserving the existing agricultural developments of the southern San Joaquin Valley by diverting the surplus waters of the Sacramento basin to the deficient areas of the San Joaquin basin. Shasta Dam, north of Redding, enables regulation of the water supply of the Sacramento River, reduces flood hazards, prevents salt-water eneroachment, and permits year-round river navigation. Incidentally, it will create a vast amount of electric power. Water will be earried to near Lathrop, where a huge punping plant in combination with extensive conduits (the Delta-Mendota Canal) will provide water for the northern San Joaquin Valley lands, now served by the San Joaquin River, and for additional undeveloped lands on the west side of the valley. This supply will permit San Joaquin waters to be stored behind Friant Dam for diversion to the southern part of the valley.

In the southern part of the state near the international boundary line, the All-American Canal carries water from the Colorado River, which is controlled by Boulder Dam, to the Imperial Valley. A branch, the Coachella Canal, will supply water to the east and west mesas and to Coachella Valley, north of Salton Sea. The Metropolitan Water District of Southern California, consisting of Los Angeles and a dozen other adjacent cities, has built a 400-mile aqueduct from the Colorado River to Los Angeles. Although the aqueduct does not now serve agricultural lands, it is potentially a water source for deficient areas in southern California.

Another problem in meeting irrigation requirements is seasonal distribution, because, since rainfall is confined mainly to the winter

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FIGURE 18. Distribution of water resources and agricultural lands. Black columns, water resources as percentages of total in state; barred columns, agricultural lands as percentages of total in state. (From Division of Water Resources Bulletin 25, 1930.)

months, the streams carry the least water when it is most needed for irrigation. Storage of water for summer and fall use has thus become necessary, and this has already been accomplished on many streams, especially in the southern three-fourths of the state. In northern and central California, irrigation or water-conservation districts have built most of the more important irrigation reservoirs; in the south, Boulder Dam is the principal one. Generation of hydroelectric power at many of these storage reservoirs is helping to reduce the cost to the irrigators.

Still another pressing problem relating to conservation of the water supplies results from a lowering of the underground waters in many parts of the state due to increased irrigation pumping. This becomes serious when the pumping draft is greater than the normal natural replenishment. It has caused most concern in the southern San Joaquin Valley, in the Santa Clara Valley, and in parts of the southern California coastal plain; but it is not confined to those areas. In a few of the coastal sections it has brought some encroachment of salt water. Overcoming this underground water shortage in the southern San Joaquin Valley is one of the major purposes of the Central Valley Project. In the Santa Clara Valley the remedial measure undertaken has been to store the excess winter flow of the principal streams, later allowing it to flow down the stream beds at such rates as will result in its absorption into the gravels and thus build up the underground supply. In the southern California coastal plain, spreading floodwaters over the porous cones which have been formed where the streams emerge from the mountains to the plains is extensively practiced. Fortunately, this problem of receding water tables is not altogether insoluble in the principal irrigated areas. It is merely an added challenge to communities dependent for their continued prosperity on conservation of water supplies, and to governmental agencies whose assistance is frequently required to accomplish that conservation.

The early work of the irrigation investigators was concerned with the immediate problems of how best to distribute and apply water and the amounts of water needed for successful agriculture. Little was known about the water requirements of crops, and there were disputes throughout the states in the arid and semiarid regions over what amounts of water should be allocated to various localities and to separate farms. This demand for information about water requirements was met by studies designed to ascertain the duty of water, that is, the amount of water necessary to irrigate lands under a given set of conditions. This includes the amount of water necessary to supply the needs of growing plants—sometimes called consumptive use—and the unavoidable transmission and evaporation losses. Although these studies provided a very necessary kind of information, they could not supply the answer to a host of important soil problems such as the following :

1. What factors determine the rate of entry of water into soil and the rate of percolation?

2. What fraction of water applied will stay in the soil and what fraction will be lost by downward percolation as a result of the pull of gravity?

3. For a given amount of water applied to the soil, how much will be lost by evaporation and how effective are the known preventive measures?

4. How available is soil water to plants and how frequently should land be irrigated?

In order to assist in answering these and many further questions, the university and cooperating state and federal agencies began, some thirty years ago, an extensive and detailed series of investigations in the field of soil and irrigation physics and soil-plant relations. These studies, while still being pursued, have had a far-reaching influence on the economic aspects of soil and water management in irrigation agriculture.

When applied from above, either by rain or by irrigation, water enters the soil at rates which depend upon the water content of the soil, the sizes of the solid particles in the soil, and their state of aggregation. In general the water enters more rapidly into coarse than into fine-textured soils, into aggregated (flocculated) than into dispersed soils, and into dry than into wet soils. The effect of soil texture is, perhaps, most striking. Laboratory experiments have shown that water may enter a sand (Oakley series) more than two hundred times as fast as it enters an adobe clay (Altamont series). An appalling illustration of the economic significance of percolation rates occurred in the spring of 1941: exceptionally heavy downpours of rain cause a temporary waterlogging in fine-textured soils of some apricot and other fruit districts, in consequence of which thousands of valuable trees succumbed within a few days.

If the soil is not uniform, but consists of distinct horizons or strata, the rate of entry of water will be changed. Obviously, if a loamy surface soil is underlain by a elay subsoil the rate of percolation will be greatly reduced as soon as the water front reaches the fine-textured layer. Curiously enough, if a loamy surface soil is underlain by a coarse-textured stratum, say a coarse sand, the rate of percolation may also diminish.

For a given soil texture, the architectural arrangement of the particles—that is, the structure of the soil—greatly affects water penetration. As mentioned earlier, floceulated soils have an open structure that favors percolation and downward movement of water, and dispersed soils make for slow movement of water. Although it is not practicable for the farmer to undertake any extensive modification of soil texture, he is nevertheless able to exert some control over the structural state of the soil. This he may do for better or worse.

An impressive illustration of the influence of soil-management practices may be seen in figure 19, which shows the relative rates of infiltration of irrigation water on the experimental plots of an orange orchard of the Citrus Experiment Station at Riverside. Treatment A consists of annual applications of one pound of soluble nitrogen per tree. Water penetration is very unsatisfactory, and at times the irrigation period must be excessively prolonged. Treatment C includes the same basic

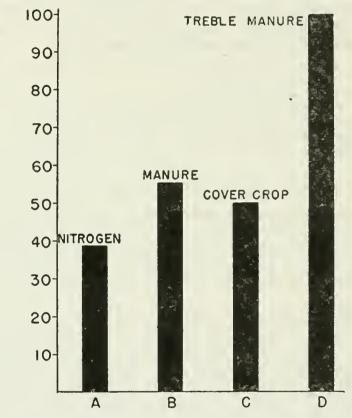


FIGURE 19. Relative rates of water infiltration on a Ramona sandy loam as influenced by organic amendments

nitrogen application as treatment A, but in addition the plot is planted every fall to a cover crop, which is turned under in the spring. The plots of treatment B also receive one pound of nitrogen per tree, but it is given in the form of stable manure. These additions of organic matter markedly improve water infiltration. The most satisfactory results are obtained with treatment D, by which amounts of stable manure corresponding to three pounds of nitrogen per tree per year are applied. Certain mineral ingredients such as gypsum, may at times also improve the rate of entry of water. Excessive cultivation may so seriously injure the structure of the soil and so much reduce the water permeability as to endanger the economic feasibility of irrigation. In a specially designed experiment, it could be demonstrated that compacting a wet Ramona sandy loam with a heavy tractor reduced the relative entry of water from 100 per cent to 7 per cent. Likewise, even on dry Ramona sandy loam, excessive use of the tractor and prolonged disking caused relative reductions of water infiltration from 100 per cent to 35 per cent and to 36 per cent, respectively. Fortunately, great improvement in water penetration on these deteriorated soils could be obtained by eliminating all cultivation for a period of years.

The study of the distribution of water in the soil immediately after its application, and the rate and extent of subsequent movement, forms an essential part of the research program of the university. Investigators have stressed the importance of the concept of field capacity, which, in general, measures the amount of water present in the soil under usual field conditions when there is a practical cessation of downward water movement. This condition usually occurs within a few days after irrigation, provided the water table is not too close to the surface. The field capacity may be estimated in the laboratory by a standardized technique which utilizes a specially constructed centrifuge. For intermediate and fine-textured soils, but not always for coarse ones, the field capacity is about equal to the moisture equivalent, the latter being defined as the amount of water a soil will retain under a centrifugal force 1,000 times gravity.

For soils having a low water table, the value obtained by subtracting the field capacity from the amount of water required for complete saturation of the soil represents approximately the amount of water that will drain away and contribute to the underground water if it percolates beyond the reach of the roots of the plants. Obviously, knowledge of the field capacity of soils constitutes an essential tool for a rational utilization of irrigation water and for proper soil conservation and watershed management. Water that is not held by the soil either runs off or moves along the bedrock and impervious strata. If it runs off, it may cause soil erosion; if it moves along the bedrock, it may cause sliding and slumping in the watershed.

Contrary to popular belief, the field capacity of soils is but slightly increased by the customary applications of organic matter such as barnyard manure. Nor does the incorporation of commercial fertilizers markedly affect the storage capacity of the soil.

Texture is the most important of the soil characteristics that control the field capacity. The following data illustrate the relation between texture and field capacity, the latter being indicated by moisture equivalent: *Moisture equivalent*

| Soil | (per cent |
|-----------------|-----------|
| Gravelly sand | 4.4 |
| Yolo sandy loam | |
| Yolo loam | 24.4 |
| Sacramento elay | 36.2 |

The table shows that the water-holding eapacity tends to be greater for fine-textured soils (elay, elay loams) than for coarse-textured soils (sands, sandy loams). Thus, 100 pounds of dry Yolo sandy loam will hold about 14 pounds of water at field capacity; the same amount of dry Sacramento elay, about 36 pounds. Conversely, a given amount of water will penetrate deeper into sands than into clays. For soils that are airdry, a convenient rule of thumb is the following: 1 inch of water over a given area will wet clay soils about 2 to 3 inches deep; loam soils, 3 to 5 inches; and sandy soils, 6 to 9 inches or more. Soils below the depth of one foot usually are not air-dry but are at the permanent wilting percentage. Under those conditions the approximate depth of penetration is obtained by doubling the values given above.

The concept of field capacity has several interesting ramifications in relation to the movement of water in soils. At or below field capacity, water moves very slowly in the soil, either under the influence of eapillary forces or under gravitational pull. For example, if a soil that is wet to the field capacity is in contact with air-dry soil, as indicated in figure 20, there will, over a period of months, be but little ehange in the distribution of water in any direction. Accordingly, water will not move appreeiably toward the roots of plants; the roots must go after the water. It has also been established that a soil area cannot be wetted throughout by surface application of water to only one part of it. If some water is added to a large amount of dry soil, the water advances into the soil in a front. Beyond the front the soil remains dry, and immediately at and behind the front the soil is wetted to field capacity. There is a sharp line of demarcation between the obviously wet soil and obviously dry soil, and this persists for many months; in other words, for all practical purposes no movement of water from the wet soil to the dry soil occurs. These findings, which are well supported by theoretical considerations, have a direct bearing on numerous soil-engineering practices and on the techniques of fertilizer experiments.

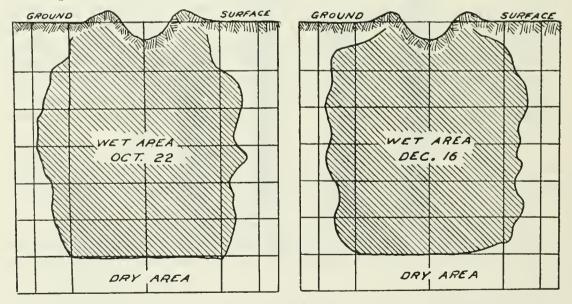


FIGURE 20. Diagrammatic representation of the slow movement of water at field capacity. The soil is a loam. After the water disappeared from the irrigation trench, a trench was cut across it and the line of demarcation between moist and dry soil was noted. The trench was then covered. Fifty-six days later, it was opened, a new face was cut, and the line of demarcation was again determined

About 1915 a series of experiments were begun for the purpose of determining in a systematic manner what becomes of the water applied to soils (pl. 3). At that time the opinion was widely held that a very large part of the water applied to soils would return to the surface by

capillary action and would be directly evaporated unless some means were employed to prevent the loss, and that one of the supposedly effective means was the maintenance of a dust mulch on the soil surface. Frequent cultivations to keep the surface soil stirred and in a finely pulverized condition had, indeed, come to be considered essential in California agriculture.

Studies carried out in widely separated parts of the state indicated. on the contrary, that the total loss of water by evaporation is very small in comparison with the losses through transpiration by plants and that in the field direct evaporation is for the most part limited to a surface layer about 8 inches thick. This layer, it is true, dries out very rapidly. But irrigation water which has passed below the top foot of soil will not return to the surface in significant amounts by direct evaporation, but only by way of plant transpiration. These findings are of great practical importance, and many orchardists have eliminated a large amount of the cultivation which, in some sections, was done once a week. In the presence of a high water table, soil mulching may conserve moisture; but in practice, by the time the soil is dry enough to permit cultivation without serious damage to its structure, the water content is at or below the field capacity and further losses by evaporation are relatively small. According to the newer ideas on soil-moisture relations, the success of bare land (fallow) in conserving moisture cannot be attributed to mulching, but must be explained by the relative ineffectiveness of evaporation to a depth greater than 8 to 12 inches, and by the elimination of losses which might occur through plant transpiration.

It has long been known that not all the water held in a soil can be extracted by plants. The fact that a soil has a high water-holding eapacity (field capacity) does not necessarily mean that it can provide plants with a large amount of water. The available soil moisture may be evaluated by calculation of the permanent wilting percentage, which is usually determined by means of sunflowers grown in pots according to a standardized technique. It represents a narrow range in the moisture content of the soil, below which plants cannot obtain water readily. At that moisture content, plants wilt to such a degree that they cannot be revived by placing them overnight in an atmosphere saturated with water. Recovery ean only be produced by the addition of water to the soil.

For a given soil series, the permanent wilting percentage is generally conditioned by the texture. If, however, soils of various series are compared, the relation between permanent wilting percentage and texture does not always hold. As a general rule, for coarsetextured soils the permanent wilting percentage tends to be below 5 per cent moisture; for fine-textured soils. 10 per cent or more. In other words, clayey soils retain more water that they will not give up to plants than do sandy soils. A elayey soil may feel rather moist, yet the plants may not be able to utilize the water.

The permanent wilting percentage of a given soil was found to be remarkably constant. Such widely different plants as grapes, alfalfa, beets, lettuce, corn, and even caeti wilt at nearly the same moisture percentage for a given soil. These rather unexpected observations are corroborated by numerous physicoehemical measurements and thermodynamic considerations, which show that the energy required to remove one gram of water from the soil is relatively small above the permanent wilting percentage, but increases enormously below that moisture range.

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For practical purposes, the amount of water between the field capacity and the permanent wilting percentage constitutes the sole water reservoir for the growth of plants. At field capacity, loams and clay loams contain from 10 to 20 per cent available water as expressed on the basis of the weight of dry soil. The values for sandy soils are usually below this range. Taking into consideration the apparent density (volume weight) of soils in their natural position, it can be stated that at field capacity most of the medium- and fine-textured soils, to a depth of one foot, will contain about one to three inches of available water. As yet, no exact rule can be given for relating the amount of available water in soils to other physical properties such as texture and porosity.

Irrigation workers at the university have gathered data which seem to indicate that plants can extract water with nearly equal ease throughout the moisture range between complete saturation and the permanent wilting percentage. These findings may serve as a guide toward the development of a rational irrigation program. Among other things, there is some uncertainty and difference of opinion concerning the advisability of frequent irrigations. In view of the evidence of uniform availability of water above the wilting percentage, there appears to be no justification for trying to keep alkali-free soils at a high moisture content throughout the period of plant growth. The quantities of water actually applied are determined by the cost of the water, the efficiency of the irrigator, the soil and its preparation for irrigation, and, finally, the character of the crop. The following seasonal applications of irrigation water have proved satisfactory on medium-textured soils under conditions of normal annual precipitation: alfalfa, 30 to 42 inches; cotton, 30 to 36 inches; rice, 60 inches; deciduous orchards, 18 to 30 inches; citrus orchards, 18 to 28 inches. The choice within these ranges will depend on locality and soil types. These figures do not include conditions existing in the Colorado Desert.

Efficiency of irrigation has been defined as the percentage of water applied that is shown in soil-moisture increase in the soil mass occupied by the principal rooting system of the crop. Water losses result from runoff from the ends of the furrows, from deep penetration, mainly at the heads of the furrows, and evaporation from the water surface and the soil mulch. The average efficiency which may be expected under good irrigation practice is about 60 per cent (San Diego County groves).

TOO MUCH WATER

While California is exerting itself to conserve water and bring it to the farmer, it must also, paradoxically, cope with a vast drainage and overflow problem. High water tables and spring floods periodically threaten the agricultural use of vast areas of fertile lands.

When, in the years 1914-1916, the water table in parts of the San Joaquin Valley rose to such heights as to endanger the irrigated agriculture, university and federal agencies undertook numerous experiments on drainage and alkali control. Simultaneously, drainage districts were organized and open-ditch drains constructed. Several hundred wells, varying in depth from 80 to 200 feet or more, were installed and pumped continuously. Marked lowering of the water table ensued. Almost coincident with this development, the state entered a cycle of below-normal precipitation. The shortage of irrigation water encouraged the use of the drainage wells for irrigation purposes. Several thousand additional wells were sunk. The result was a complete disappearance of poor drainage conditions in many parts of the valley.

The introduction of irrigation to the Imperial Valley and the Palo Verde Valley was accompanied by immediate needs for drainage. In the Palo Verde Valley, marked success was obtained with deep open drains, since a permeable sandy layer exists there at depths of from three to eight feet below the surface. In the Imperial Valley the fine texture and intricate stratification of the alluvial deposits has prevented equally successful attempts at drainage.

In the past, spring floods and overflows along the major streams have presented problems to agriculture that have taxed the skill of our best engineers. The Saeramento River and its main tributaries used to overflow vast areas of flat lands at times of excessive rains and much melting of snow in the Sierra. By now, from as far north as Chico almost to its lowest reaches it is leveed and regulated by an elaborate system of weirs and by-passes. Likewise, the entire Delta region is leveed against overflow from the Saeramento and San Joaquin Rivers, the major tributaries of which also are controlled by extensive levees.

Reclamation enterprises also protect the lands of Tulare Lake, and areas adjacent to numerous overflowing streams such as the Eel, Russian, Salinas, Santa Maria, Santa Clara, Santa Ana, and Los Angeles Rivers. Spectacular by reason of their magnitude and cost are the works for the prevention of overflow of the Los Angeles and San Gabriel Rivers and the protection of the adjacent deusely populated and highly industrialized parts of the Los Angeles metropolitan area. Significantly enough, these control measures are not restricted to the lower ends of the rivers where overflows actually occur. They extend clear to the sources of the streams-the watersheds in the mountains. Elaborate devices for measuring transpiration rates by various trees and shrubs, for studying evaporation of water from soils, and for controlling infiltration rates and runoff have been installed by the United States Forest Service in various parts of the steep, rugged, and chaparral-covered slopes of the Los Angeles and San Gabrial watersheds. This scientifically planned project represents a vital and promising coordination of soil science, forestry, and flood control.

TILLAGE, DEEP OR SHALLOW?

In Colonial times, when Pennsylvania was the wheat granary of the nation, the farmers plowed "at the most four, but more frequently less than three inches deep." As late as 1820 five- to seven-inch plowing was called "deep" in the east, and apparently was frowned upon, for, as an observer says, "They deem it a great evil to turn up the red earth." The wooden plow was fragile and the oxen were slow. The average rate of plowing was only three-fourths of an aere in a day, a day then meaning from sun to sun.

California skipped this period, for the most part. When the fortyniners poured in, the east-iron plow was in wide use in the east and John Deere in Moline, Illinois, had begun to turn out his famous steel plow commercially. Immigrants on wagon trails and elipper ships sailing round the Horn brought the plows to California.

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Local toolmakers immediately began competing. Stockton gang plows became popular; special plows for tule and adobe lands were constructed; also subsoil plows, and many others specially adapted to the soil and crop conditions of the state—for example, the sugarbeet plow. A recent curiosity is the giant plow in Orange County, 16 feet long, that plows to a depth of 56 inches and turns over a strip of land about 4 feet wide.

In the late 'sixties, wheel plows, or sulkies, and gang plows were much more in evidence on the Pacific Coast than elsewhere. Gang plows were used for second, or fallow, plowing and for cross-plowing. They plowed shallow and were good for burying wheat seed. In the 'eighties the eight-horse unit drawing two gangs with four bottoms each were typical in the San Joaquin and Sacramento Valleys. They cultivated, on the average, six acres a day. Steam-tractor plowing on bonanza farms was much publicized but was a minor element in California wheatgrowing.

Western farmers were impatient with the slowness of the plow. They experimented with rotary spades, screw pulverizers, and rotary harrows. Finally, since the turn of the eentury, disk harrows have broken the dominance of the plow in California. Simultaneously, spring-tooth harrows and cultivators became popular. Since 1920, the offset harrow has been used in many orchards and vineyards. It permits cultivation under the trees without getting the tractor too elose to the trunks. A recent development is the basin lister, which is used in water- and soilconserving activities.

Very early in California history the idea of deep tillage and clean and frequent cultivation was advocated by the farm press, "regardless of changing ideas and styles of experiment stations and colleges." In particular, Warren and Son, owners of the *California Farmer*, undertook a vigorous campaign to promote subsoiling. In the first volume of that journal (1854) the editors frequently directed attention to the moisturesaving possibilities of intensive cultivation. "The greatest feature of advancement in agriculture in California, is deep plowing. We do not hesitate to say, that the cost of waterworks of all kinds for the purposes of irrigation that could be saved by deep plowing, even the present year, would be more than the cost of supporting the government."

The testimonials published in favor of "stirring the earth as a relief against drought" are astounding. An article written by J. Lowell and republished in the *California Farmer* includes the following remarks: "The severe drought threatened the total loss of the potato erop. On one of the hottest and driest days I gave them a thorough plowing. In three days after, the potatoes changed their color, they started afresh as if they had received the benefit of ample showers, while not a drop of rain had fallen."

It is no wonder that the idea of deep and intensive eultivation became widespread among California farmers. A lively controversy arose between the proponents of "skinning" and of "gutting." Accordingly, the first field experiment ever undertaken by the university (1875, by Hilgard) was to determine the comparative effects of deep and shallow plowing. Owing to various difficulties the results were not conclusive. It is only within the past two decades that the problem of soil moisture has been sufficiently clarified—as described in the preceding sectionto permit a rational formulation of tillage methods in relation to moisture conservation.

Deep tillage as a means of breaking up plow soles, plow pans, elaypans, and hardpans—without, however, bringing the subsoil to the surface—is furthered by the Killefer system. This, though also known as subsoiling, panbreaking, or chiseling, should not be confused with deep plowing.

In orchard management there is at present a trend away from deep tillage. Heavy disks that penetrate deeply cut too many feeder roots. Although this may be of minor concern in deep alluvial soils, it assumes damaging proportions on soils having dense subsoils that crowd the tree roots toward the surface. Disk harrows are now provided with depthcontrol appliances which permit setting the disk gauge at full angle to cut all the weeds, yet prevent penetration to a depth of more than four or five inches.

Even compete elimination of tillage has been advocated. A permanent furrow system naturally would prevent plow-sole formation and its disastrous effects on water penetration. In fact, one of the finest citrus orchards in the south has had no cover crop and has not been cultivated for the last twenty years.

THE MENACE OF SOIL EROSION

Although soil erosion had long been a pressing problem in the agriculture of the state, it did not have the active attention of the university until the beginning of 1930, when interest was stimulated through participation by the federal government in matters pertaining to soil and water conservation throughout the country. Erosion in California differs somewhat from that in other parts of the country, but in certain places is no less extensive or severe.

Here, the agricultural soils enter the rainy season nearly or wholly devoid of active vegetative ground cover. Since the surface of the soil is poorly protected, it suffers from the impacts of torrential rains. Almost all the sloping agricultural lands have been damaged by erosion. In some, the loss is small and inconsequential; in others, large and irreparable. The level areas, although themselves not significantly eroded, are frequently damaged by the deposition of eroded materials from adjacent slopes.

California soils differ greatly in their susceptibility to crosion. Soils having pervious surface layers but impervious subsoils (elaypans) erode much more easily than soils uniformly pervious or uniformly impervious. In some soils occurs the so-called sheet crosion, by which there is a rather uniform loss of surface soil over considerable areas; in others, deep and spectacular gullies are formed. The most crosive soils are in the D group of the natural land classification. These soils occupy the higher coastal terraces and include such series as Olivenhain, Las Flores, and Tierra. Many soils of the E group (upland soils), especially if their slopes exceed about 15 per cent, also are subject to serious crosion.

In the past decade the search for effective methods of erosion control has brought about significant changes in cultural practices and in soil manipulation. With the aid of terraces, check dams, and diversion ditches, engineers mechanically retard or divert the flow of water. The agronomists try to achieve the same goal by improving and stabilizing the vegetational ground cover. Dense growth of grasses and cover crops have been very effective in erosion control, on both irrigated and nonirrigated areas. Where permanent ground cover is not convenient, the introduction of "stubble mulch fallow"—the stubbles not being plowed under but merely chopped up with a disk—has given good results. On uncultivated lands, controlled grazing by curtailment of the number of animals, or rotation grazing, or the planting of new grasses, has been beneficial.

Under California law, farmers in any community may organize soil-conservation districts under the leadership of the United States Soil Conservation Service. These encourage cooperation in soil conservation and give aid to the farmer which he might not be able to obtain by himself.

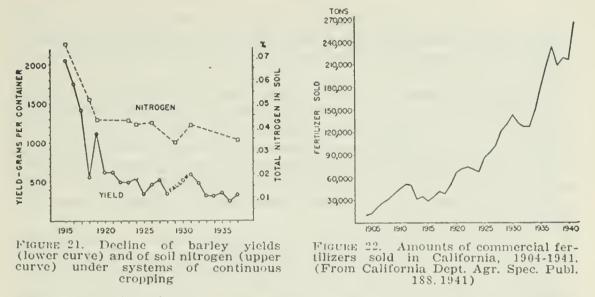
EVALUATING THE FERTILITY OF CALIFORNIA SOILS

When Sutter established New Helvetia in 1839 and dreamed of an agricultural empire in the Sacramento Valley, he had good reason for being optimistic. Back-home, in Switzerland, people were on starvation diets. Land there had been in cultivation for centuries; it was worn and exhausted, and the crop yields were low. But here in California lay millions of aeres of virgin land ready to release to mankind their pent-up fertility that had gradually accumulated since the land was formed.

Indeed, early California crop yields were high: "Vegetables raised here would astonish you both as to quantity and quality-cabbages 53 pounds per head, Irish potatoes 33 inches in circumference, etc., wrote George McKinstry, Jr., to Lieutenant Kern in 1851. J. B. Croekett, in a lecture in San Francisco in 1854, exclaimed : "In spite of droughts and floods and winds and fogs, the virgin soil yielded such bounteous returns as had hitherto been wholly unknown in any part of the world, and were in fact so marvellous as to challenge belief in their reality." Wheat yields were 40 to 50 and even 70 bushels per acre. (At present, 25 to 30 bushels is considered exceptionally good.) Nevertheless, California signified no exception to the general principle that cultivated soils sooner or later decline in their productive capacity unless correc-tive measures are applied. In the 'eighties, Hilgard said : "The need for fertilization may be expected to arise within from five to twenty years, according to the nature of the land, and the kind and intensity of production thereon. In a few cases this need will be found to exist at once."

For the study of the exhaustion of soil fertility under controlled conditions, large quantities of thirteen California soils were brought to Berkeley in 1915 and placed in open galvanized-iron containers. The soils were continuously cropped to Beldi barley. No fertilizer was added. During twenty-five years of observation all these soils revealed the same story: a continuous decline in yield and a corresponding reduction in some of the chief constituents of soil fertility, such as nitrogen. A representative set of data is shown in figure 21. Whereas the decline was very rapid at the beginning, it became less marked in ensuing years. It appears that these soils tend to reach a low but stable level of productivity.

That the need for augmenting soil fertility must be widespread in California is corroborated by the phenomenal rise in the consumption of commercial fertilizers from 1904 to 1941, shown in figure 22. This



gives a forceful picture of the farmers' efforts to build up inherently poor soils and to counteract the declining productivity of the land. It does not follow, however, that the farmer has always been successful in attaining his objective, for the buying of fertilizer is often governed by a mixture of facts, fables, and salesmanship.

While the rate of increase of fertilizer consumption is impressive, the actual amounts used are still small, considering the acreage of land

| Crop | Tons | Crop | Tons |
|--|---|--|--|
| Citrus fruits Lettuce Potatoes Celery Deciduous fruits Ornamentals Meions Sugar beets | 85,000 36,000 25,000 22,000 15,000 9,000 6,700 6,400 | Field crops Nuts Peas Rice Peppers Hops Avocados, dates, olives Vegetables other than mentioned | 4,000 4,000 3,700 2,000 1,500 1,260 |
| Berries Cotton Grapes Tomatoes | 5,000 5,000 5,000 5,000 | above Other crops Total | 14,10 6,38 265,04 |

Table 3. Approximate tonnages of commercial fertilizers used on various cropsin California in 1941.

Source of data: California U.S.D.A. War Board, War Letter No. 140, June, 1942.

on which a response might be secured. In 1941 the amount of commercial fertilizer sold was 265,043 tons, representing an expenditure by the farmers of more than \$11,000,000.³ The amount was distributed among crops as shown in table 3. It is difficult to determine to what extent this fertilizer was used wisely. It may be stated with respect to California soils in general that nitrogen is usually deficient, that phosphorus is deficient for some field and truck crops in many places, and that the number of soil series with known potassium deficiency is rather limited.⁴ There is no direct evidence indicating a widespread and urgent need for complete fertilizers for many of the crops grown commercially in California; yet California sales of so-called "complete mixed fertilizers"

³ In 1948 the amount sold reached 548,744 tons.

⁴ Extensive field and pot experiments indicate large areas of phosphate deficient soils.

amounted in 1941 to 88,000 tons. The university strongly encourages the application of fertilizers for California soils. It places emphasis on research for rational use in accordance with the needs of the plant and of the soil.

The establishment of a sound and economical fertilizer program is an individual farm problem in which crop, soil type, climate, previous cropping, and soil-management practices are the important factors. Obviously it is impossible to maintain a scientifically controlled experiment field on every part of every farm in the state. Hence the university has long engaged in an intensive study of the scientific principles which underlie crop production, though without losing intimate contact with the needs of the practical farmer.

Properly conducted field trials are highly important; but they are very costly, since variability of soil, fluctuations in seasons, and the visitations of plant diseases and pests demand much replication and repetition; and furthermore, irrigation technique is difficult to standardize. The most elaborate scientifically controlled field experiment anywhere in the state is conducted at the Citrus Experiment Station at Riverside. Begun in 1917, it uses an area of some 50 acres and employs more than 40 different treatments. The experiment is still in progress and is contributing much valuable information to eitrus growers.

Numerous test plots are scattered over the state. These may be merely demonstrations to convince farmers of a fertilizer response known to occur in the district, or they may be simple tests designed to explore a given situation. In 1940 the university supervised approximately 500 demonstrations and tests dealing with commercial fertilizers.

In the absence of field experiments, pot tests may be of assistance in determining the fertility level of soils. For such tests the soils are brought to greenhouses and placed in pots holding from 20 to 400 pounds each. Nutrient elements, singly or in combination, are added, and plants are grown under standardized conditions. The cost of these tests is low in comparison with that of field experiments. The relatively small amount of soil used per plant readily discloses the first limiting nutrients of the soil. The main disadvantage lies in the uncertainty of extending the results to field conditions. The degree of uncertainty is sometimes small and sometimes very large.

In chemical laboratory tests, soil samples are treated with various solvents and the amounts of readily available nutrient elements are determined by analysis.⁵ Results are obtained quickly and cheaply, and a large number of soils can be tested. The main difficulty lies in the correlation of these tests with field data. Furthermore, scientists have not yet been able to determine how accurately these extraction methods simulate the action of plant roots.

For this reason, biological laboratory tests have been perfected. Plant seedings or microorganisms are grown on small soil samples and, after a few days or weeks, are analyzed for their nutrient content. Thousands of such chemical and biological tests have been run on California soils. Comparisons of the biological method and the chemical extraction tests reveal the interesting fact that, for a large number of

⁵ A promising chemical test for available soil phosphorous has been published in Bingham, Frank T., Soil test for phosphate: California Agr. Exper. Sta. Bull., vol. 3, no. 8, pp. 11, 14, 1949.

California soils, plants such as rye seedlings extract much greater quantities of potassium than is indicated by chemical tests (exchangeable potassium). These unexpected findings are a challenge to the scientist, because a proper understanding of the basic problems of soil fertility cannot be had unless the mechanism of mineral intake by plant roots is fully clarified. Plant-nutrition specialists of the university are investigating various phases of this fundamental problem. They have found that the nutrient uptake is not a mere physicochemical process, but is intimately associated with the activities of the living protoplasm in the root. In particular, the metabolic processes are stimulated by the presence of oxygen—a fact that throws new light on the importance of adequate soil aeration. An outgrowth of these studies has led to the commercial development of water culture, or hydroponies.

In recent years a new method of estimating fertilizer requirements has received much attention. In analyzing thousands of plants and plant parts for their nutrient content in the course of the past hundred years, soil scientists and plant physiologists have found that both the total ash content and its composition vary widely with soil conditions and climate. Of relatively recent origin is the assertion that there exists a critical concentration of nutrients in certain plant parts that is indicative of the nutrient needs of the entire plant. At or below this concentration, plant growth will be stimulated by additions of the corresponding fertilizer materials. The critical concentration is thought to be nearly independent of soil type and climate. If this suggestion should prove generally valid, the analysis of specific plant parts would become very important in estimating the fertilizer needs of a growing plant. The university is actively engaged in fostering this new development.

WHAT HAPPENS TO FERTILIZERS WHEN ADDED TO SOIL?

Like the efficient industrialist who keeps track of every phase of the manufacturing process, the California farmer, who is something like a biological engineer, wants to know the fate of the millions of dollars' worth of fertilizer he annually incorporates into the soil. A significant part of the university's research in soil chemistry and soil microbiology is connected with this very question. Whereas earlier studies centered mainly around the transformation of nitrogen, more recent trends focus attention on the phosphate problem. A few of the discoveries which have practical importance may be noted here.

Nitrogen in the form of nitrate (NO_3) , as in Chilean nitrate, has been found not to react with the solid parts of the soil. Consequently, it is readily carried into the subsoil by penetrating water and under excessive irrigation may be lost by filtration into deep strata.

Nitrogen in the form of ammonium ions or ammonia (NH_4^+, NH_3) , as in ammonium sulfate or liquid ammonia, is held by the colloidal soil particles, where it may be readily available. In fine-textured soils such as elay loams it may not penetrate below the surface inch or two of soil. Soon after fixation, however, soil bacteria will convert the ammonia and ammonium forms of nitrogen into the nitrate form, and subsequent rains or irrigations will carry the nitrates into the subsoil.

If nitrogen is added to the soil in organic form, such as stable manure and cover crops, these materials will be decomposed by microorganisms, especially bacteria, fungi, and actinomyces. When urea is used, soil enzymes may be involved directly. Ultimately the nitrogen will be converted to nitrates. In this form it can be used advantageously and economically by terrestrial plants. The rate of conversion depends on a large number of factors, the most prominent being the kind of microbes present in the soil, conditions of moisture and temperature, soil reaction, and the carbon-to-nitrogen ratio of the organic materials.

In fertilizer practices that employ phosphates, the concept of availability assumes prime importance. For instance, although some representatives of Yolo clay loam and of Aiken clay loam soils contain almost the same amounts of total phosphorus—2,100 and 2,000 p.p.m. PO₄, respectively—they differ widely in available phosphate. Dilute sulfuric acid will extract 1,100 p.p.m. PO₄ from the Yolo soil, but only 130 p.p.m. from the Aiken soil. Rye seedlings (Neubauer test) will remove 150 p.p.m. of phosphate from the former and only 24 p.p.m. from the latter. Most field crops do well on Yolo clay loam, but fail to grow on Aiken clay loam unless phosphates are supplied.

Phosphates added to the soil in such forms as superphosphates and ammonium phosphates react readily with the soil particles and therefore penetrate very slowly into lower strata. In the presence of lime, the soluble phosphates are precipitated as relatively insoluble calcium phosphates. In order to liberate these phosphates for plant use, the roots must produce acids (hydrogen ions) in amounts sufficient to create localized zones of phosphate dissolution.

Some soils, especially those—such as the Aiken series—having kaolinitic types of colloidal particles, fix phosphates by an adsorption mechanism which renders the phosphates exceedingly unavailable, and consequently large amounts of phosphate fertilizer must be added to promote plant growth. The entire chemistry of phosphate fixation and phosphate availability is extremely complicated. In spite of notable advances made by university investigators, much yet remains to be done.

Potassium fertilizers react with colloidal clay and humus particles by means of an exchange process:

Clay
$$Ca + K_2SO_4 \Rightarrow Clay = \frac{K}{K} + CaSO_4$$

Potassium ions displace the calcium ions on the surface of the clay particles and take their place. These "adsorbed" potassium ions do not move readily with penetrating water, and therefore the rate of distribution of potassium ions within the soil mass is rather slow. Yet these adsorbed ions can be readily utilized by plants and are nearly as available as if they were in true solution. This phenomenon has been designated as "contact effect." It is believed that the ions on the clay particles may react directly with the root surface when the latter comes into close proximity to the clay surface.

But in some California soils the potassium, after having been adsorbed on the clay particles, undergoes a further change. Apparently it is being locked up, perhaps in the interior of the clay crystal, because it is no longer available to the plant. It cannot be exchanged or displaced by the ordinary ion-exchange methods. Soils that possess this trapping mechanism offer a serious obstacle to potassium fertilization because as soon as the fertilizer is added the potassium becomes unavailable and no plant response results.

RESTORING SOIL NITROGEN AND ORGANIC MATTER

In virgin soils there exists a delicate balance between gains of nitrogen through bacterial activity and losses through the decomposition of organic materials. When man removes the natural plant cover and cultivates and crops the land, this equilibrium is disturbed and nitrogen losses are increased.

Just when the need for replenishing nitrogen was first felt in California, it is difficult to say. No records are on hand that would indicate any directed use of animal manure in the agriculture of the mission period. Old settlers maintained that "manuring is too costly and will never pay." When Hilgard came, in 1875, he was fully conscious of the possibilities of nitrogen deficiencies. He initiated field experiments, some pot tests with sodium nitrate, and numerous chemical soil analyses, in attempts to explore the nitrogen problem. He concluded, however, that in California soils nitrogen would probably not be among the first ingredients to be exhausted. "So far as our observations go," he wrote, "it is likely to become deficient next in order to phosphorie acid under normal conditions and should be supplied whenever the superphosphates fail to produce satisfactory results." Now, half a century later, nitrogen is considered to be the first limiting element for most California soils.

The field experiment at the University of California Citrus Experiment Station at Riverside lends itself admirably for a systematic inquiry into the nitrogen problem. The average relative yields (1928-1939) of oranges for various types of nitrogen fertilizers were as shown in the following summary: Relative yield

| No. | Treatment | (per een |
|-----|---|------------|
| 6 | Cover erop only (no nitrogen added) | _ 45 |
| 27 | Sodium nitrate with cover crop | _ 100 |
| 28 | Sodium nitrate and gypsum with cover crop | _ 105 |
| 21 | Calcium nitrate with cover crop | $_{-}$ 106 |
| 15 | Ammonium sulfate with cover crop | _ 97 |
| 18 | Urea with cover crop | _ 100 |
| 17 | Dried blood with cover erop | _ 101 |
| 43 | Cottonseed meal with cover crop | |
| | Dairy manure with cover crop | |
| 30 | Dairy manure without cover crop | 99 |
| | | |

With the exception of the plots having a cover crop only (no. 6), all plots received nitrogen amounting to 1 pound of nitrogen (N) per tree annually. All were used with cover crop except one of the dairy-manure treatments. There are 91 trees to the acre. The mean annual yield of the sodium nitrate plots was 126 pounds of oranges per tree for the period under consideration. This value is given a relative rating of 100, and all other yields are expressed in proportion to this arbitrary standard.

The summary discloses that the annual addition of 1 pound of nitrogen per tree has more than doubled the yield on this soil, a Ramona loam. Similar responses have been observed in a large number of citrus orchards. It makes no difference, within the limits of experimental errors, in what form the nitrogen is given; nitrates, ammonium compounds, and several different organic materials are equally effective. Only dairy manure in combination with cover crop exhibits a signifieantly lower value. This equality of nitrogen carriers in the presence of cover crops has been observed in many other citrus orchards and in numerous deciduous orchards also. It may be well to emphasize that

(t)

none of these treatments had any adverse effect on the commercial quality of the fruit.

The deficiency of nitrogen, so serious in a large number of the eitrus orchards, is less pronounced for deciduous-tree orehards. The results of a number of experiments conducted, mainly by the university, in the years 1926-1933, are given in table 4. Nitrogen amounting to 0.45 to 2.00 pounds per tree was applied as ammonium sulfate or sodium nitrate. The response to nitrogen was variable. Only three times out of seven was there a significant increase in yield. It is not known whether this differential behavior of deciduous and citrus trees is conditioned

| Fruit and locality | Duration | Average on check plots | Increase of yield on nitrogen plots |
|---|----------|------------------------------|---|
| | years | pounds per tree | per cent |
| Peaches: Modesto | 5 | 241 | 31 |
| Santa Clara Valley | 3 | 269 | 0 |
| Merced County | 6 | 216 | 4 |
| Prunes: Woodland Santa Clara Valley | $5\\4$ | 243 84 | $\frac{4}{22}$ |
| Pears: Lakeport | 6 | · | 26 |
| Apricots: Santa Clara Valley | 4 | 209 | 5 |
| Grapes: Alexander Valley | 5 | 3.65* | 5 |

Table 4. Results of nitrogen fertilization of deciduous trees.

* Tons per acre.

mainly by the physiology of the trees or by the type of soil on which they are grown.

On a large number of California soils, field crops and truck erops respond readily to nitrogen, although to a degree varying with soil type, erop, and soil management. For purposes of illustrating the variety of conditions and the complexity of the soil and plant relations a few typical trials are enumerated.

In pot experiments, ammonium sulfate at the rate of 500 pounds (100 pounds of nitrogen) per acre increased the yield of potatoes in Yolo sandy loam near Santa Maria by 34 per cent. In the field the same rate of application produced a yield increase of 190 per cent on Hesperia sandy loam at Shafter, where potatoes are a failure unless fertilized with nitrogen.⁶ Significant responses have also been obtained on Standish sandy loam at Susanville, but not on peat soil at Tulelake.

Tomatoes reacted favorably to nitrogen fertilization on Yolo silt loam, Rincon soil, Pinole loam, Montara clay loam, and Brentwood elay, under both field and pot trials.

In the Salinas Valley, farmers used to add 100 to 200 pounds of ammonium sulfate per acre to sugar beets. Higher amounts were considered excessive and likely to produce beets with a low sugar content.

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⁶ They respond more readily to ammonia-nitrogen than nitrate-nitrogen.

Field experiments showed, however, that 1,500 pounds of ammonium sulfate gave significant increases in yield without lowering the sugar content. Moreover, in pots holding 500 pounds of soil (Metz silty clay loam), ammonium sulfate corresponding to 2,400 pounds per acre increased the yield from 695 grams to 3,200 grams of clean beets per pot. This enormous production was accompanied by increases in sugar content and degree of purity. Under the favorable conditions of light and temperature that prevailed throughout the experiment, all nitrogen taken up by the roots was utilized for growth. At harvest time there were no free nitrates in the leaves and consequently no reduction in the sugar content of the beets.

Lack of nitrogen often limits the growth of the lettuce plant. On Hanford sand and on Hanford sandy loam, 60 or 120 pounds of ammonium sulfate stimulated production by 100 to 130 per cent, but sodium nitrate had no effect. No benefits from nitrogen applications were observed on Yolo silty clay loam and on various types of the Salinas series.

Sweet corn reacted favorably to nitrogen on Indio very fine sandy loam, but not on Burns elay loam.

Many small-grain crops, such as wheat and barley, respond satisfactorily to nitrogen fertilizer on a wide variety of soils. In 1940, trial plots scattered over the state showed that in 39 out of 50 tests wheat or barley definitely benefited from nitrogen application; but in 1941 only 7 out of 21 new tests reacted positively to nitrogen. In many localities, barley planted after fallow will not respond to nitrogen fertilization.

In some parts of Europe where agriculture is most intensive the use of animal manure is considered the key to successful farming. How it is that the nature of the constituents of barnyard manure and their mode of action might explain the leading role of this soil amendment is a question that has not yet been answered satisfactorily. Since many erops, especially tomatoes, potatoes, corn, wheat, and even fruit trees, ean be grown in excellent condition and to full maturity in artificial nutrients solutions, without additions of organic matter, one is forced to conclude that the beneficial effect of manure is not caused by any mysterious constituent in it. Likewise the successful maintenance of productive orchards without the use of manure or cover crops suggests that organic matter may not always be as indispensable as once was thought. There is now a tendency among many agriculturists to attribute the indisputable beneficial effects of organic manures to their content of nutrient elements, on the one hand, and to the influence of the organic substances on the physical and chemical properties of the soil, on the other. Organic matter is also important in supplying energy materials for the activities of the microörganisms in the soil.

The most extensive and painstaking field experiments on the effect of manure and cover crop on the productivity of California soils have been conducted by the University of California at Riverside. During the twelve-year period 1928-1939, the application of one pound of nitrogen per tree produced the following average annual yields of oranges per tree :

| Nitrogen as nitrate or as urea | 111 | pounds |
|---|-----|--------|
| Nitrogen in the form of dairy manure | 125 | pounds |
| Nitrogen as nitrate or urea, plus cover crop turned under | 129 | pounds |

Dairy manure increased the yield of oranges by nearly 13 per cent. This beneficial effect cannot be attributed to the content of phosphorus and potassium, for additional experiments demonstrated that these two elements do not affect the yield on this soil. The presence of a cover crop increased the efficiency of nitrogen fertilization by 16 per cent.

The differences in yield would probably have been much greater had not all plots been periodically sprayed with zinc compounds to prevent the mottle-leaf disease. Before zinc spraying was begun in 1934, the trees on the clean-culture plots were much more seriously affected with mottle-leaf than those on the comparable cover-cropped plots. In the period 1923-1935, there were some years when the clean-culture plots fertilized with sodium nitrate and with calcium nitrate yielded 35 and 38 per cent, respectively, less than corresponding cover-cropped plots. Zinc applications cured practically all the mottle-leaf by the summer of 1935 and eliminated its depressing effects on yields.

The organic amendments in the form of either stable manure or cover crop had very striking and visible effects on the physical properties of the soil. The lack of organic matter in the nitrogen-fertilizer plots resulted in a compact soil which absorbed water slowly. The penetration and movement of irrigation water was greatly restricted in these plots.

Generally speaking, the economic merits of manure will vary widely with its nitrogen content and price. The cost of growing a winter cover crop and the possible inconvenience it entails, especially if the orchard has to be heated, have retarded its use as a universal practice. The advantages, however, may greatly outweigh the disadvantages, if the beneficial effect of the cover crop on the trees and on the yields of fruit are high enough. Lastly, the value of winter cover cropping as an effective means of preventing soil erosion is definite and widely recognized, though hard to evaluate in dollars.

Experiments conducted from 1909 to 1915 on Sierra sandy loam at the old Rubidoux Station (Riverside) illustrate the comparative merits of leguminous and nonleguminous winter cover crops on the yield of succeeding field crops. The annual tonnage of green manures (fresh weight) at the time they were turned under averaged 9 tons per acre for nonlegumes (barley, rye, alfilaria) and 12 tons for legumes (vetch, bur clover, Canada peas, *Melilotus indica*, and others). After the winter cover crops had been turned under, summer field crops were planted in March or April, according to variety and season. The average yields are shown in table 5.

Effects of the leguminous crops were, without exception, markedly beneficial. The percentage increase for all crops (including sorghum hay and Sudan grass hay) for six years is 38 per cent in favor of the legumes.

In the University of California's experimental deciduous fruit orchard at Davis, cover crops, either leguminous or nonleguminous, did not measurably alter the total nitrogen content of the soil over a period of ten years. At Riverside, with large lysimeter tanks, legume cover crops gave an increase of 75 to 100 pounds of nitrogen per acre per year (six-year average) over nonlegumes, when both were turned under in spring. This nitrogen gain from legumes was reflected, first, in increased yields of harvested crops, and second, in increased leaching losses of nitrogen. In accord with the findings at Davis, the permanent nitrogen content of the soil was not increased by the legumes.

| Nature of cover erop | Shelled corn | Potatoes | Bects | Cabbage |
|----------------------|--------------|-----------|-----------|-----------|
| | (5 crops) | (2 crops) | (2 crops) | (2 crops) |
| | pounds | pounds | pounds | pounds |
| | per acre | per acre | per acre | per acre |
| Nonlegumes | 1,708 | 9,732 | 24,601 | 10,124 |
| | 2,486 | 13,588 | 30,741 | 15,377 |

Table 5. Yields of field crops after green manures.

The statement that, per unit of nitrogen, all organic materials are about equally effective requires qualification. Some consideration must be given to the proportions of nitrogen and carbon in organic fertilizers. While manure, cottonseed meal, and dried blood produced similar orange yields, large incorporations of cereal straw, even in the presence of one pound of nitrogen per tree, reduced the yield by 16 per cent.

Microbiologists attribute the depressing effect of cereal straw to the activity of microörganisms. During the decomposition of organic matter, the soil bacteria and fungi utilize nitrogen for their own growth and metabolism. If the proportion of carbohydrates to nitrogenous substances is large, most of the nitrogen will be in the bodies of the microbes and consequently the plant roots will be temporarily deprived of available nitrogen. Presumably, the more the carbonto-nitrogen ratio in organic fertilizer exceeds the value 10 to 1, the slower is the rate of decomposition of the material and the rate of mineralization of the nitrogen compounds. The unfavorable performance of bulky organic fertilizers having wide carbon-to-nitrogen ratios often may be overcome by supplements of mineral nitrogen fertilizers. These newer microbiological ideas on the availability of soil nitrogen may offer an explanation of Hilgard's old observations on the nitrogen hunger of humus. He recommended the use of nitrogenous fertilizers such as Chile saltpeter for any soil containing humus with much less than 2.5 per cent of nitrogen-even if the total nitrogen content of the soil is high.

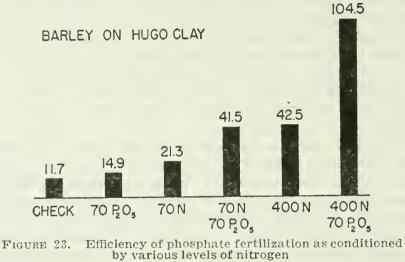
Similar phenomena are encountered in crop-rotation practices. Special studies have been conducted on the effect of corn and sorghum on succeeding crops. Sorghums usually produce marked injury to succeeding nonleguninous crops, whereas corn seldom does so. Studies conducted by the university suggest that part of the injury must be attributed to the high sugar content of the sorghum residues, which stimulates the growth of microorganisms. Greenhouse and field studies lend support to the theory that lack of available nitrogen is the immediate cause of the injury to the succeeding crop. In replicated plots at Davis and El Centro for three years, applications of sodium nitrate and ammonium sulfate have markedly increased the yields of the crops following sorghums, the increases being roughly proportional to the rate of application.

THE COMPLEXITY OF PHOSPHORUS RESPONSES

In a paper on "Improvement and Fertilization of Land." published in 1894, Hilgard stressed the phosphate deficiency of California soils. "It happens," he wrote, "that in California most of the rocks—and therefore the soils derived from them—are poor in phosphates. Hence, phosphates are among the first ingredients to become deficient in California soils; as has been amply proved by actual experience of farmers, in whose hands superphosphates and phosphatic guanos have become the favorite fertilizers from the first." Authorities on fertilization give phosphorus second place, today, in the order of fertilizing elements for California soils.

Perhaps Hilgard did not have enough information to justify his state-wide generalization. It is possible, however, that the accelerated exhaustion of soil nitrogen since the turn of the century is a eause of the change in fertilization policy. The following brief account of an experiment may help to make clear the interplay of nitrogen and phosphorus in plant production.

In pots, nonfertilized Hugo elay seeded to barley produced the very low yield of 11.7 grams (fig. 23). Additions of treble superphosphate at the rate of 70 pounds of P_2O_5 per acre increased the yield to only 14.9 grams, which is statistically not significant. Nitrogen alone (70 pounds per acre) nearly doubled the output, giving a yield of 21.3 grams. When both nitrogen and phosphorus were applied, the yield was again doubled,



becoming 41.5 grams. Thus, in the absence of nitrogen the phosphate fertilizer was inactive, but in the presence of nitrogen it produced a significant increase in yield. Furthermore, when the amount of nitrogen added was raised from 70 pounds to 400 pounds per acre, the 70 pounds of P_2O_5 increased the yield from 42.5 grams (with 400 pounds of nitrogen) to 104.5 grams, which represents a gain of 250 per cent. Similar relations were observed in the field, with lettuee grown on Greenfield coarse sandy loam. Nitrogen alone (120 pounds per acre) or phosphorus alone (120 pounds of P_2O_5 per aere) had no effect on the yield, but the combination of the two fertilizers increased it significantly. It is to be noted, therefore, that the need for a given fertilizer may be concealed by one or several other limiting nutrient elements. This possibility must be given serious consideration in the planning of field experiments.

The current belief that phosphorus is not limiting in most California soils is mainly justified by the performance of tree crops.⁷ Scientifically conducted field experiments by the university with oranges, peaches, prunes, apricots, and grapes on such soil series as Ramona.

⁷ It is now recognized that, excepting for tree crops and vines, phosphorus is low in many California soils.

Sierra, Hanford, Placentia, San Joaquin, Porterville, Yolo, Corning, and Aiken failed to show any significant yield increases from phosphate application, either in the absence or the presence of nitrogen (0.6 to 4 pounds of nitrogen per tree.) In spite of this essentially negative information, many citrus growers annually apply large quantities of phosphate materials to their groves. Consequently, the soils of citrus orchards in various localities have made important gains in phosphate content, as was shown by a comparison of 49 orchards with their near-by unfertilized lands.

Field crops and truck crops present an entirely different picture.⁸ On the Aiken elay loam, characteristically low in available phosphorus and having a high fixing power for this element, the yield of cherries, prunes, almonds, peaches, walnuts, and apples is very good; and furthermore, heavy applications of phosphates have not, so far, produced any changes in yield, quality of fruit, or tree growth. On this same soil and in the same locality (Paradise), eighteen field and truck crops such as corn, beans, alfalfa, lettuce, and barley failed to make satisfactory growth unless large amounts of phosphate were added. For example, in 1940, the yield of potatoes, when no phosphate was added, was 4 tons per acre. Nitrogen alone gave little or no increase. When phosphate alone was added (2,200 pounds of P_2O_5 per acre), the yield rose to 12 tons. Phosphate in combination with nitrogen produced 17 tons.

The exact reason for the differential behavior of trees and annual erops is not fully understood. On an acre basis, the phosphate removal by an average erop of oranges plus that required for the production of the annual new growth of the trees is not greatly different from that removed by small grain, corn, clover, and potatoes. But whereas the annual crops must obtain their phosphates in a growing period of from 2 to 4 months, citrus trees probably absorb phosphate continuously throughout the year. Similarly, the root activity of deciduous fruit trees under California conditions appears to continue throughout the winter.

With soil types that are not as deficient in available phosphorus as the Aiken clay loam, the responses to field crops vary greatly. Field experiments (1937-40) with Ladino clover, a legume, on San Joaquin loam near Oakdale showed an average yield of dry matter amounting to 1.61 tons per acre. Treble superphosphate at the rate of 69 pounds of P_2O_5 per acre produced an increase of 84 per cent. On the same soil type, near Galt, 54 pounds of P_2O_5 per acre increased the yield of Ladino clover only 8 per cent. Phosphate in conjunction with calcium has proved especially effective. From 1938 to 1940 the average annual yield produced by the addition of 1,000 pounds of hydrated lime per acre was 1.43 tons of dry clover per acre. The addition of 65 pounds of P_2O_5 per acre increased the average yield by 126 per cent. On Elkhorn sand at Watsonville, 180 pounds of P_2O_5 per acre increased the yield of peas (clean peas) 33 per cent in 1939 and 81 per cent in 1940. Beans on the same soil also profited from phosphate fertilization.

Of sixty-one state-wide tests with small grains conducted in 1940 and 1941, only eight showed a definite superiority of phosphorus and nitrogen over nitrogen alone. In the remaining fifty-three the response was negative or inconclusive.

⁸ Truck crops often respond to phosphorus during the cool winter season. Proper placement of fertilizer also was found to be important.

With potatoes on Hesperia sandy loam at Shafter, treble superphosphate (90 and 180 pounds of P_2O_5) in the presence of 150 to 200 pounds of nitrogen produced yield increases of from 9 to 15 per cent during the years 1937-39, but had no effect in 1940 and 1941. On Metz silt loam near King City, sugar beets did not respond to phosphates in the presence of nitrogen. Lettuce yields on Greenfield coarse sandy loam increased more than 200 per cent upon application of ammonium sulfate (120 pounds of nitrogen per acre) and treble superphosphate (120 pounds of P_2O_5). The responses were nil on the Salinas and Hanford series. Sweet corn on Burns clay loam benefited greatly from superphosphate.⁹

LIMITED RESPONSES OF CROPS TO POTASSIUM FERTILIZATION

In scientifically controlled fertilizer tests very few California soils have revealed serious deficiencies in potassium. Usually, as with phosphorus, the plant's needs for nitrogen must be satisfied before its potassium requirements become evident.

The following responses to potassium fertilizers, mainly in the presence of nitrogen and phosphorus, have been obtained in field experiments conducted by the university :

Yield increase

| Crop, | soil | type, | and | locality | |
|-------|------|-------|-----|----------|--|
| | | | | | |

| Orop, som type, and toouting | (per cent) |
|---|------------|
| Oranges : Ramona loam, Riverside | 1 |
| Hanford sandy loam, Arlington | |
| San Joaquin sandy loam, Jasmine | |
| Porterville clay loam, Porterville | |
| Yolo loam, Fullerton | |
| Hanford sandy loam, Orange | |
| Placentia loam, Arlington Heights | |
| Peaches: | |
| Fresno sand, Modesto | 7.5 (?) |
| Merced County (soil type not recorded) | |
| Prunes : | |
| Woodland (soil type not recorded) | 0 |
| Pinole loam, Morgan Hill | |
| Farwell loam, Chico | . Marked |
| Pears, Lakeport (soil type not recorded) | _ 0 |
| Grapes, Corning gravelly loam, Alexander Valley | _ 10-20 |
| Potatoes: | |
| Hesperia sandy loam, Shafter | _ 0 |
| Peat, Tulelake | _ 0 |
| Sweet potatoes, Ramona fine sandy loam, Orange County | _ 0 |
| Sugar beets, Metz silt loam, Soledad | _ 0 |

| | Number of | Number of soils, in per cent | | |
|---|--|------------------------------|--------------------------------|--|
| Soil group | soils tested | Low in available nitrogen | Low in available phosphorus | |
| Recent alluvial soils Older alluvial soils Claypan soils Hardpan soils Soils of hills and mountains | $ \begin{array}{r} 121-137\\ 81-91\\ 59-65\\ 27\\ 96-110 \end{array} $ | 55 56 71 48 68 | $38 \\ 42 \\ 71 \\ 74 \\ 67$ | |

⁰ On the basis of pot tests using lettuce plants as indicators, nitrogen and phosphorus deficient soils have been elassified as follows: Jenny, H., Vlamis, J., and Martin, W. E., Greenhouse assay of fertility of California soils: Hilgardia, vol. 20, no. 1, 8 pp., May 1950.

| Crop, soil type, and locality | Yield increase (pcr cent) |
|--|------------------------------|
| Canning peas, Elkhorn sand, Watsonville | . 0 |
| Ladino elover, San Joaquin sandy loam, Oakdale | 0-100 |
| Lettuce: | |
| Salinas series, Salinas | |
| Hanford sandy loam, Salinas | . 0 |
| Greenfield coarse sandy loam, Salinas | 0 |
| Tomatoes, Brentwood clay, Brentwood | . 0 |
| Onions, Fresno fine sandy loam, French Camp | 0 |

Positive effects were obtained with prune trees, grapes, and Ladino clover, but only on certain soils. Pot experiments with field crops reveal a similarly inconsistent situation. The problem resolves itself into a systematic search for those specific soil series and types which are definitely deficient in potassium.

In California, potassium deficiencies are most conspicuously manifested in connection with "prune dieback" in the northern Sacramento Valley. As noted earlier, trees that had thrived during the first five to eight years in the orchard developed a sudden scorching of the leaves and a subsequent dying-back of limbs. Sometimes entire trees died, and this resulted in abandonment of some of the land given over to prune production.

Field and laboratory trials conducted by the university indicated that prune dieback was associated with soils which not only were frequently low in potassium, but also exhibited a marked ability to fix this element. This is especially troublesome with deep-rooted crops like trees, since fixation by the surface soil when the fertilizer is broadcast over the ground makes it difficult to get the potassium down to the root zone. A method of injecting dissolved potassium fertilizer into the soil to a depth of three feet was devised. Trees so treated remained healthier than adjacent untreated trees.

Soils in the northern Sacramento Valley that are low in potassium should not be planted to prune trees. If the biological "Neubauer test" indicates less than 125 p.p.m. potassium to a depth of three feet, scorch and dieback conditions may develop. In the orchards already established, improvement may be expected from additions of potassium if this is placed in the deeper soil. The American Potash Institute reports such improvement on Honeut clay loam, Pinole loam, and Rincon clay loam. Cultural practices for reducing the losses in established orchards have been mentioned earlier in this volume.

SOIL REACTION, AND IRON AND SULFUR DEFICIENCIES

The possible influence of soil reaction on plant growth occupied the attention of the university staff as soon as the proper techniques for measuring acidity were made available. Contrary to expectations, the relatively low degrees of acidity that are characteristic of most of the state's arable soils were found to have no detrimental effects on the yields. Likewise, the fantastic claims of specific optimums of soil reaction for each crop species, which still appear in pamphlets and circulars, could not be supported by experiments with nutrient solutions having known and controlled degrees of acidity. On the alkaline side of soil reaction, which is widespread in the state (see fig. 15), the hazards of growing plants are more clearly manifested. While moderate degrees of alkalinity do not seem to harm roots directly, certain indirect effects may become of much concern to the grower; namely, decreased availabilities of phosphates and of iron in the presence of lime excesses, and possibly the precipitation of such micronutrient elements as zinc, copper, and manganese.

The leaves of some plants when growing in soils containing excess lime become more or less yellow—a condition caused by iron deficiency and known as lime-induced chlorosis. Lime in excess interferes with the absorption and utilization of iron by the plant, even though the soil contains (as it often does) an abundance of iron. The more common commercially cultivated susceptible trees are the pear, apple, quince, peach, apricot, prune, plum, cherry, orange, lemon.¹⁰ A lime content of 1.0 per cent or more is likely to cause chlorosis of certain trees, especially pear trees, and a content of 0.5 to 1.0 per cent may be viewed with suspicion.

The only practical, immediate cure for lime-induced chlorosis is to apply iron in suitable form and amount directly to the plant. Four successful methods may be used : first, trench application, by which soluble iron salts are strewn along the bottom of trenches one to two feet deep around the tree; second, spraying of iron solutions on the leaves of the trees; third, injecting solutions of iron salts into the trunk; and fourth, placing dry, soluble iron salts in holes bored in live wood and subsequently sealing the opening with a suitable wax.

When correct treatment is applied, the effect is evident in the first year in a heavier set of fruit, amounting to as much as 100 per cent increase over that of untreated trees. In the second and third years, chlorosis gradually shows again and treatment has to be repeated.

Since 1918, many tests for sulfur deficiency have been conducted on alfalfa and other crops. Remarkable responses followed the addition of sulfur, or sulfur and lime, or gypsum to many soil types in Humboldt, Mendocino, Tehama, and Yuba Counties and the sandier soils in Stanislaus and Merced Counties. In Butte, Shasta, Siskiyou, Lassen, and Modoc Counties, definite, and often marked. responses occurred in alfalfa and in irrigated pastures consisting mainly of Ladino clover.

In the southern part of the state no sulfur deficiencies have been found with subtropical crops. Probably the continued supply provided by the sulfate of irrigation waters and the sulfur contained in various insecticides and commercial fertilizers satisfy the needs of the plants. On the nonirrigated, reddish upland soils (Sespi series) of Ventura County, however, bur-clover pastures benefited greatly from sulfur applications.

DISCOVERY OF MICRONUTRIENT ELEMENTS, AN AWARD TO RESEARCH

Some years ago, observations began to indicate that the classical and time-honored list of the ten essential elements (carbon, oxygen, and hydrogen from air and water; nitrogen, potassium, phosphorus, calcium, magnesium, sulfur, and iron from soil) is incomplete, and that additional chemical elements are indispensable to plant life. Those discovered in a number of pioneering investigations conducted by the university and

¹⁰ Also almond and walnut.

by other institutions are zine, copper, manganese, boron, and, very recently, molybdenum. The distinguishing feature common to these elements is that, unlike all but iron on the classical list, they are required by the plant in exceedingly small amounts. Thus, the amounts of molybdenum necessary to insure satisfactory growth of plants in nutrient solutions are as small as one part of molybdenum in a hundred million parts of water.

The extremely low order of magnitude of the requirements of micronutrient elements by higher plants and the exacting technical procedures necessary for their study in the laboratory may lead one to question whether deficiencies of micronutrients are ever likely to be encountered in the field, in plants grown in soil. The answer is emphatically yes.

In 1931 and 1932, four groups of workers, one of them at the university, discovered independently that treatment with zine will cure a serious orehard disease that occurs from Florida westward through the Gulf states, Texas, Arizona, and California, and northward at least to the Canadian line. Many millions of dollars' worth of land otherwise excellent for orchards are almost worthless for this erop unless zine is supplied to prevent or cure the disease. On the pecan and the apple it is called rosette; on the citrus fruits, mottle leaf; on the walnut, yellows; and on grapevines, stone-fruit trees, and some other trees, little-leaf.

All orchard and ornamental trees and shrubs grown in the valleys of California seem to show injury if the zine deficiency is great enough, but differences in susceptibility are large. The most susceptible tree seems to be the sweet cherry, which may die from insufficient zine where trees of all other kinds are healthy. Then following, roughly in order of susceptibility, are the apple, the Japanese plum, possibly the European plum, the peach, the walnut, the apricot, the avocado, citrus fruits, some varieties of grapes, the fig.¹¹

In California, soils on which trees are most apt to show zine deficiency are sandy or gravelly. Trees on compact elayey soils rarely show it except where there have been old corrals, or where there has been heavy manuring as for hotbeds or truck growing, or where there have been Indian eamps.

Many of the soils on which trees die unless treated are exceptionally good for annual plants and alfalfa. Apparently we have here a reversal of the condition encountered with phosphates.

Soils containing zine sometimes fail to supply enough for trees. Analyses showed that there were more than 3,000 pounds of zine per acre in one soil which produced strong zine-deficiency symptoms in trees. Yet, during seven years of growth this orchard had removed little more than one-half pound of zine to the acre in roots, tops, and fruits.

Soil treatments tend to be more effective the nearer the zine compound is placed to the trunk of the tree. In a soil with low fixing power for zine, 1,000 pounds of zine sulfate to the acre spread over all the soil cured nearly all the trees and kept them healthy for about three years; but 300 pounds to the acre all within two feet of the trunks was more uniformly effective and the benefit lasted as long.

Many soils have so high a fixing power for zine that zine treatments by way of the soil become ineffective. According to laboratory studies, the

¹¹ Also the almond, the pear, and the pecan.

fixing power of certain types of soils for zine appears to be closely correlated with the type of minerals they contain. Minerals containing magnesium, and kaolinitic colloids, were found to be especially effective in rendering zinc unavailable.

Experience in treating trees aboveground by spraying (10 pounds of zine sulfate with half as much hydrated lime in 100 gallons of water), or by driving pieces of zinc into them, shows that without any change in the soil or in the supply of zinc to the roots of zinc-deficient trees these roots are capable of supporting at once a strong growth in the top. For example, in March, 1934, grapefruit trees were sprayed with zinc. The crop on the unsprayed trees amounted to 56 pounds each; that on the sprayed trees, from blossoms that opened only a few weeks after the spraying, 477 pounds each, and the individual fruits were 66 per cent larger, the yield being expressive of the greatly increased and healthy foliage. In one whole orchard, about thirty acres of mature navel orange trees, the crop harvested the first autumn after a January spraying with zinc was said by the owner to be six times as large as the orchard had ever yielded before. Results almost as striking have followed dormant spraying of deciduous fruit trees with zinc sulfate. In a large number of districts in the Sacramento, San Joaquin, and other Valleys, and notably in the citrus belt, orchards are now regularly treated with zinc.

Alfalfa grown in pots on a Hanford sandy loam from the vicinity of Santa Ana was found to be responsive to additions of manganese. In culture solutions and in sand cultures, symptoms of manganese deficiency could be induced in citrus leaves, in which they show a close resemblance to the symptoms of the early stages of zinc deficiency (mottle-leaf). Manganese-deficiency symptoms have been observed widely on citrus and walnuts and sometimes on peaches and apricots in the southern part of the state; also on almond, apple, pear, cherry, plum, prune.12

In many localities throughout the state, citrus, apple, and pear ¹³ suffer from exanthema, a disorder caused by copper deficiency. The disease is being combated by spraying. Very small doses, as little as onefourth gram per tree, have restored normal growth.

Boron deficiency has been observed in some trunk crops, apple trees, and numerous olive trees, in the latter especially when grown on the Aiken soils.14

¹² Sprays are now being used.

¹³ Also plum, walnut, and olive.
¹⁴ It also occurs on the pear, plum, and walnut.

COMMERCIAL FERTILIZERS

BY WILLIAM E. VER PLANCK

Commercial fertilizers, as defined in Section 1022 of the Agricultural Code of California, are substances and mixtures of substances containing 5 percent or more of nitrogen, available phosphorus pentoxide, or potassium oxide soluble in distilled water, singly, collectively, or in combination, except manures, hays, straws, peat, and leaf mold. Manures are classified separately for the purpose of controlling sales.

Conventionally the total nitrogen content of a fertilizing material is designated by the symbol N. Usually nitrogen is further designated as nitrie nitrogen, ammonic nitrogen, and organic nitrogen. The symbol P signifies the percent of available P_2O_5 (soluble in ammonium citrate), and the symbol K signifies the equivalent percent of water-soluble K_2O .

Commercial fertilizers confprise one of five classes of fertilizing materials defined by the Agricultural Code. This body of law, which is administered by the State Bureau of Chemistry, is intended to protect the consumer from worthless or harmful materials. The requirements of the law differ in detail for each elass of fertilizing material, but included among the regulations covering the sale of commercial fertilizers are the following:

- 1. Each lot or parcel offered for sale must bear a label with the following information :
 - a. Name or brand name of the product.
 - b. Name and address of producer, importer, or dealer.
 - e. Place of manufacture.
 - d. Chemical analysis.
- 2. Every producer, manufacturer, or importer must obtain a certificate authorizing the registrant to sell commercial fertilizers.
- 3. The Bureau of Chemistry is authorized to take samples and make tests to determine if the commercial fertilizer conforms to the guarantee.
- 4. A tonnage tax on sales and registration fees are authorized.

In 1949 sales of commercial fertilizer in California amounted to 511,460 tons containing 93,120 tons of nitrogen, 45,670 tons of available P_2O_5 , and the equivalent of 10,300 tons of K_2O , or a total of 149,090 tons of plant food. The following table¹ indicates the relative quantities of materials sold as commercial fertilizers in California during 1949.

Although materials containing a single plant food are used in appreciable quantities, most commercial fertilizers contain two or three plant foods. Such a fertilizer may be a chemical compound or a mixture containing several of the materials enumerated above. Mixed fertilizers, which are intended to supply the total plant food requirements of a particular soil, sometimes contain inert material in addition to the active ingredients. This may be a soil conditioner such as ground gypsum or limestone, a carrier, or a diluent such as sand or earth. Mixed fertilizers are usually prepared close to the consumer.

The grade of a mixed fertilizer is customarily designated by a formula such as 10-10-5 in which the first figure indicates the percent of

¹ Based on data in Fertilizing materials: California Dept. Agr., Special Pub. 236, 1949.

| Material | Short tons | Percent by weight of total |
|----------------------------|------------|-------------------------------|
| Mixed fertilizers, dry | 154,787 | 30.2 |
| Ammonium sulfate | 80,167 | 15.7 |
| Single superphosphate | 56,725 | 11.1 |
| Ammonium nitrate | 52,016 | 10.2 |
| Ammonium phosphate-sulfate | 38,611 | 7.5 |
| Liquid fertilizers | 25,353 | 5.0 |
| Calcium nitrate | 14,664 | 2.9 |
| Organic fertilizers | 12,449 | 2.4 |
| Ammonium phosphate | 8,745 | 1.7 |
| Urea | 6,783 | 1.3 |
| Sodium nitrate | 5,488 | 1.1 |
| Calcium cyanamide | 5,126 | 1.0 |
| Potassium salts | 4,523 | 0.9 |
| All others | 46,203 | 9.0 (by dif- |
| | , - | ference) |
| Total | 511,640 | 10.00 |

Commercial fertilizers-1949.

nitrogen present as nitric nitrogen, ammonic nitrogen. and/or organic nitrogen. The second figure indicates the percent of available P_2O_5 (soluble in ammonium citrate), and the third the equivalent percent of water-soluble K₂O. The material in this example therefore contains 10 percent nitrogen, 10 percent available P_2O_5 , and 5 percent equivalent K₂O. It must be emphasized that two fertilizers having the same formula may have different properties and uses. Over a hundred grades of mixed commercial fertilizer are on the market, but ten grades account for over three-quarters of the tonnage sold in California. These are 10-10-5, 17-7-0, 8-8-4, 6-10-4, 8-10-12, 6-9-6, 4-10-10, 15-8-4, 10-20-0, and 10-10-10.²

Most commercial fertilizers are dry granular or powdery materials, but a small but increasing tonnage of liquid fertilizer is being used as additions to irrigation water. A liquid fertilizer may be a single chemical or a solution containing several chemicals.

The materials described in this paper are those employed as commercial fertilizers in greatest abundance. They may be used singly or in mixtures.

Ammonium Sulfate. Ammonium sulfate $((NII_4)_2SO_4)$, a fine crystalline powder, is a favorite nitrogen material containing between 20 and 21 percent ammonic nitrogen. It is produced by neutralizing synthetic ammonia with sulfuric acid:

$$2\mathrm{NH}_3 + \mathrm{H}_2\mathrm{SO}_4 \rightarrow (\mathrm{NH}_4)_2\mathrm{SO}_4$$

Ammonium sulfate crystals are recovered from the solution by vacuum evaporation followed by centrifuging and drying to remove water. Ammonium sulfate used in California is made in this way by the Shell Chemical Company at Shell Point, California, and the Consolidated Mining and Smelting Company at Trail, British Columbia. The Kaiser Company produces a smaller amount as a by-product of coke manufacture at Fontana, California.

Ammonium Nitrate. Ammonium nitrate (NH_4NO_3) is a soluble material containing more nitrogen than does ammonium sulfate. The average nitrogen content of the ammonium nitrate sold in California

² Op. cit., p. 15.

1951]

during 1949 was 16.81 percent animonic nitrogen and 16.78 percent nitrie nitrogen, totalling 33.59 percent. Agricultural ammonium nitrate is mixed with ground limestone or ammonium sulfate because of the hygroscopic and explosive properties of the pure salt. It is made by reacting nitric acid with ammonia:

$$\mathrm{HNO}_3 + \mathrm{NH}_3 \rightarrow \mathrm{NH}_4 \mathrm{NO}_3$$

The ammonium nitrate is recovered from the solution by evaporation and granulated. The Hercules Powder Company produces some at Hercules, California. Much of that used in California is "Nitrapills" made by the Consolidated Mining and Smelting Company at Trail, British Columbia. This granular product is made in a tower by spraying an ammonium nitrate solution downward against a rising current of air.

Urca. The urea of commerce is a manufactured organic chemical having the formula $NH_2 \cdot CO \cdot NH_2$. Natural urea is an ingredient of manure. The pure material is a soluble white crystalline powder containing 46.7 percent nitrogen, more than most other common compounds. The urea used in California for agricultural purposes is "Uramon" manufactured by the DuPont Company at Belle, West Virginia, and it contains 42 percent nitrogen. Urea is manufactured by reacting anhydrous ammonia with carbon dioxide and water in an autoclave at 100 atmosphere pressure and 190° C. The reaction takes place in two stages:

 $CO_2 + 2NH_3 \rightarrow NH_2CO_2NH_4$ (ammonium carbamate) $NH_2CO_2NH_4 \rightarrow NH_2 \cdot CO \cdot NH_2$ (urea) + H₂O.

The reaction which is about 80 percent complete, takes several hours. *Calcium Nitrate*. Calcium nitrate $(Ca(NO_3)_2)$ is prepared by

neutralizing nitric acid with limestone:

 $CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$

The ealcium nitrate precipitate is granulated and usually mixed with ammonium nitrate to reduce eaking. Calcium nitrate is imported from Norway, and the material sold in California contains 14.7 percent nitric nitrogen and 0.8 percent ammonic nitrogen.

Sodium Nitrate. Sodium nitrate $(NaNO_3)$ a soluble, somewhat hygroscopic, white salt, is prepared from natural nitrate deposits in Chile. Formerly sodium nitrate was an important source of nitrogen, but its use has declined in recent years. Artificial sodium nitrate is not used as a commercial fertilizer in California. In Chile the crude ore or caliche, which contains between 5 and 30 percent sodium nitrate, is first leached with hot unsaturated liquor. The nitrate-rich liquor is then chilled, and the sodium nitrate crystals that form are recovered from the mother liquor with Dorr thickeners. A non-caking product is made by melting and spraying the crystals. In this way tiny pellets with a glazed surface are formed. Sodium nitrate sold in California contains 16 percent nitric nitrogen.

Calcium Cyanamide. Calcium cyanamide $(CaCN_2)$ is a powdery black material that has some use as a fertilizer. That sold in California contains between 20 and 22 percent nitrogen. It is manufactured at Niagara Falls, Ontario, by treating finely ground calcium carbide (CaC_2) with nitrogen at a temperature of from 1600° to 1800° F:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

The reaction, which is exothermic, takes place in a firebrick-lined steel shell of 1600 pounds capacity. The heat necessary to start it is provided by an electric resistance element placed in the center of the charge. Twenty to 40 hours are required to complete the reaction. The product is crushed and ground, sprayed with water to remove traces of ealcium carbide, and treated with oil to reduce dustiness. Much of the calcium cyanamide produced at Niagara Falls is used to make organic chemicals.

Agricultural Ammonia. Agricultural ammonia, the most concentrated of all the nitrogen-bearing commercial fertilizers, is produced by the Shell Chemical Company at Shell Point, California. It contains 81 percent ammonic nitrogen, and it is employed by mixing it with the irrigation water or by injecting the gas into the soil with special equipment.

Phosphorous Compounds. Almost all phosphorus-bearing commercial fertilizers are manufactured from western phosphate rock, a material commonly considered to have the formula $(CaF)Ca_4(PO_4)_3$. Untreated phosphate rock is generally considered too low in available P_2O_5 for use as a commercial fertilizer, and several methods of making the phosphorus available have been perfected.

For agricultural purposes phosphate compounds are classified according to their solubility. Water-soluble compounds, which are available to plants, include monocalcium phosphate $(CaH_4(PO_4)_{\circ})$. monammonium phosphate $(NH_4H_2PO_4)$, diammonium phosphate $((NH_4)_2HPO_4)$, and some organic phosphates. Insoluble compounds, that are not available to plants, include the tricalcium phosphate $(Ca_3(PO_4)_2)$ present in phosphate rock, the mineral apatite, and the phosphate in bones. Plants are able to make use of some phosphate compounds that are not soluble in water. It happens that solubility in ammonium eitrate is an empirical test of the availability of phosphate compounds to plants, and ammonium citrate-soluble phosphate is ealled available phosphate. Those compounds insoluble in water but soluble in ammonium citrate include dicalcium phosphate (CaHPO₄) and the phosphate present in basic slag and fused phosphate rock.

Phosphoric acid, made either by treating phosphate rock with sulfuric acid or in electric or blast furnaces, has some application as a liquid commercial fertilizer. That sold in California contains 52 percent available P_2O_5 . Much larger quantities are used in the manufacture of other phosphate fertilizers.

Single or normal superphosphate is the oldest of the processed phosphates and is still the most important. It is made by treating ground phosphate rock with sulfuric acid :

 $\begin{array}{ccc} 2((\operatorname{CaF})\operatorname{Ca4}(\operatorname{PO4}){}_3) + 7\operatorname{H}{}_2\mathrm{SO4} + 17\operatorname{H}{}_2\mathrm{O} \rightarrow 3\operatorname{CaH4}(\operatorname{PO4}){}_2\mathrm{H}{}_2\mathrm{O} + 2\mathrm{HF} + 7\operatorname{CaSO4}{}_2\mathrm{H}{}_2\mathrm{O} \\ & \operatorname{Phosphate\ rock} & \operatorname{monocalcium\ phosphate\ } gypsum \end{array}$

The hydrogen fluoride reacts with silica and water to form fluosilicic acid (H_2SiF_6) ; this is sometimes recovered. The final product is a mixture of monocalcium phosphate and artificial gypsum with some dicalcium phosphate and a trace of free phosphoric acid.

Much single superphosphate is made by the Den process, a batch process in which the mixed ingredients are dumped into a briek or concrete "den" of 100 tons capacity or more. After staying in the "den" for from 6 to 24 hours the material may be cured by leaving it in stock piles for up to 10 weeks. In an alternate method the material from the "den" is granulated and conditioned by water spraying followed by drying. The conditioning is followed by a curing period of only 10 days.

A continuous process is used at a few plants. The reaction takes place in a tower into which phosphate rock is introduced as dust and sulfuric acid as a fine spray. The reacted materials are withdrawn from the base of the tower in the form of a thin slurry. It is conditioned mechanically and further cured in stock piles.

Single superphosphate, because of dilution with gypsum, contains but little more than 18 percent available P_2O_5 . The gypsum has, however, some value as a soil conditioner. Plants manufacturing single superphosphate in California are located at Richmond and at Vernon.

Triple superphosphate is a much more concentrated material containing from 42 to 46 percent available P_2O_5 . It consists almost entirely of monoealcium phosphate. Phosphate rock is treated with phosphorie acid in processes similar to those used for making single superphosate:

 $(CaF)Ca_4(PO_4)_3 + 7H_3PO_4 + 5H_2O \rightarrow 5CaH_4(PO_4)_2H_2O + HF$

Triple superphosphate plants are located outside of California elose to supplies of raw materials.

Ammonium phosphate fertilizers are manufactured by the Consolidated Mining and Smelting Company at Trail, British Columbia. One product is made by neutralizing phosphoric acid with anhydrous ammonia:

 $H_3PO_1 + NH_3 \rightarrow NH_4H_2PO_4$ (monoammonium phosphate)

The slurry of ammonium phosphate that forms is granulated and dried for shipment. This product, containing 11 percent ammonic nitrogen and 48 percent available P_2O_5 , is known as 11-48-0 ammonium phosphate.

A second product is called ammonium phosphate-sulfate or 16-20-0 ammonium phosphate. It is made by a process like that used to produce 11-48-0 ammonium phosphate except that a mixture of phosphoric acid and sulfuric acid is neutralized with ammonia. Some ammonium sulfate is added to the acids before neutralization.

Potassium. The potassium of commercial fertilizers used in California is almost entirely potassium salts manufactured by the American Potash and Chemical Corporation from the complex brine of Searles Lake, San Bernardino County. Treatment of the Searles Lake brine is discussed in the section on the minerals of commercial fertilizers. Potassium sulfate containing 51 percent equivalent K_2O and potassium chloride containing 60 percent equivalent K_2O are produced. Most of the agricultural potassium finds its way into mixed fertilizers, but some potassium chloride and potassium sulfate are used alone.

Although Searles Lake is the principal current source of potash in California, a Bay area producer markets a potash-bearing material made from cement mill dust. Most of the material comes from dumps at the Henry Cowell Line and Cement Company plant at Cowell, Contra Costa County, but some is obtained from the Santa Cruz Portland Cement Company plant at Davenport, Santa Cruz County. The product is guaranteed to contain 2 percent equivalent K_2O although some specimens contain as much as 15 percent equivalent K_2O .

Organic Fertilizers. Organic fertilizers include several processed waste materials, many of which are intended primarily for animal feed. They are comparatively low in plant food. Slaughter house products include blood meal, bone meal, and tankage. Blood meal, which contains about 13 percent nitrogen, is made by cooking blood until it has coagulated. The solids, after separation from the liquid, are dried and powdered. Bones are cooked to remove grease, erushed, and powdered to form bone meal containing 1 percent nitrogen and up to 16 percent available P_2O_5 . Tankage, a brown meal containing 7 to 9 percent nitrogen and 1 to 3 percent available P_2O_5 is prepared from meat scraps, intestines, hoofs, bones, condemned carcasses, and similar waste. These substances are first cooked with steam to remove grease and tallow. The solids are then ground and washed with naptha to remove any remaining grease. Fish meal, prepared in a similar way from fish scraps, contains about 10 percent nitrogen and from 4 to 8 percent available P_2O_5 .

Seed meal is pomaee or the pulp remaining after the oil has been pressed from cotton seeds, castor beans, soy beans, peanuts, or apricot kernels. It contains up to 7 percent nitrogen, 1 to 3 percent available P_2O_5 , and up to 2 percent equivalent K_2O .

Included with the commercial fertilizers is guano. Bat guano contains about 10 percent nitrogen, 3 percent available P_2O_5 , and $1\frac{1}{2}$ percent equivalent K_2O .

Activated sewage sludge which may contain up to 6 percent nitrogen and 2 percent available P_2O_5 , qualifies as a commercial fertilizer. Sewage sludge is, however, discussed in more detail in the section on agricultural minerals.

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MINERALS OF COMMERCIAL FERTILIZERS

BY WILLIAM E. VER PLANCK

OUTLINE OF REPORT

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INTRODUCTION

California possesses adequate reserves of some of the raw materials used in commercial fertilizers but is dependent on out of state sources for other important materials. For phosphates, California is entirely dependent on phosphate rock brought in from Wyoming, Idaho, and Montana. For nitrogen compounds, the entire world depends largely on atmospheric nitrogen fixed by artificial means. Three ammonia plants in the San Francisco Bay area supply a large part of California's requirements. California production of potash is far in excess of consumption. The state's output, which amounts to between 10 and 15 percent of the total United States production of potash, is from a single plant at Searles Lake, San Bernardino County.

NITRATES

No commercial deposits of natural nitrogen compounds have been found in California, although traces of sodium nitrate occur in certain playas and in efflorescent deposits throughout the southeastern desert. An exhaustive search of these occurrences, undertaken during World War I and in following years, failed to find commercial deposits. No further work was done during World War II when there was a shortage of nitrogen compounds.

The present most important source of nitrogen compounds is synthetic ammonia (NH_3) . In the presence of a catalyst and under proper conditions of pressure and temperature hydrogen is made to combine with nitrogen. Two of the three California plants obtain hydrogen from natural gas; the third uses by-product hydrogen from the electrolysis of salt. Ammonium sulfate and ammonium nitrate are made from synthetic ammonia in the San Francisco Bay area, and a small amount of ammonium sulfate is produced at Fontana, San Bernardino County, as a byproduct of coke manufacture. Imports of ammonium sulfate, ammonium nitrate, and calcium cyanamide (CaCN₂) come from Canada; and calcium nitrate comes from Norway. Natural sodium nitrate is imported from Chile although in smaller quantities than before World War H.

PHOSPHATES 1

Occurrences of phosphates are known in California, but commercial deposits have not been developed.

Phosphorus in the crust of the earth is involved in a complex geologic evele, several stages of which are represented by commercial deposits of

¹The section on phosphates is essentially a direct quotation from Braun, L. T., Phosphates, in Mineral Commodities of California; Calif. Div. Mines Bull. 156, pp. 189-192, 1950. Certain parts of Mr. Braun's article having no direct bearing on commercial fertilizers have been condensed and rearranged.

phosphates. This cycle begins with the entry of magmatic phosphorus into the minerals of igneous rocks, principally apatite $(Ca_{10}F_2(PO_4)_6)$. A few deposits of apartite occur in sufficient concentrations and quantity to be economic sources of apatite. The cycle is continued when phosphorous, leached from crystalline rock by weathering, enters the soil as phosphoric acid. Much of this phosphoric acid is absorbed by plants and in turn by animals. Some of these animals, notably bats, sea birds, and seals, contribute to guano deposits which are an important source of phosphate.

Ultimately most of the phosphorus reaches the sea and is deposited in marine sediments. The factors involved in marine phosphate deposition are not completely understood. Marine organic agencies undoubtedly play a part, but direct chemical precipitation is also believed possible. Marine beds ranging from slightly phosphatic marks and limestones to phosphate rock containing as much as 90 percent tri-calcium phosphate have been deposited over large areas. A deposit of this type is represented by the Permian Phosphoria formation which is exposed in portions of Utah, Wyoming, Idaho, and Montana. Concentrations of phosphate rock in this formation are the source of the phosphate processed and consumed in California. At the present time phosphate rock containing over 65 percent tri-calcium phosphate is considereded workable.

Phosphate rock is composed almost entirely of collophane, a carbonated calcium phosphate. Collophane is considered by Rogers² to be an amorphous mineraloid of fairly definite composition; Frondel³ believes that collophane is a submicrocrystalline variety of apatite.

Under certain conditions low grade phosphatic limestones may be weathered in such a manner that calcium carbonate is removed in solution, and residual deposits of phosphate rock accumulate. The Florida deposits, from which two-thirds of the United States production and almost half of the world production are derived, are an example of a residual deposit, in part reworked.

Under other conditions surface waters may leach phosphate accumulations and redeposit the phosphate at lower levels, enriching pre-existing deposits or forming new ones. The guano deposits of the Pacific islands have been leached in this manner, and commercial phosphate deposits have been formed in the underlying coral limestone. To complete the phosphorous cycle, marine beds may be buried and metamorphosed to again form crystalline apatite.

In California grains of apatite occur in igneous rocks, notably in those of the San Gabriel Mountains. Nodules and pellets of collophane are found in Tertiary marine sediments and in sediments forming at the present time off the California coast. The presence of these nodules indicates that commercial deposits of phosphate rock might possibly be found in the Tertiary sediments of the state.

In the Carmel Valley, two poorly defined phosphate-bearing beds occur in Miocene shale. The beds, which are about half a mile apart, vary from 6 inches to 1 foot in thickness and are composed of pellets that may be microcoprolites. Collophane onlites or pellets are often found in the Miocene sediments of the southern San Joaquin Valley and the Los

²Rogers, A. F., Collophane, a much neglected mineral: Am. Jour. Sci., 5th ser., vol. 3, no. 16, pp. 269-276, 1922. ³Frondel, Clifford, Mineralogy of the calcium phosphate in insular phosphate rock : Am. Mineralogist, vol. 28, pp. 215-232, 1943.

Angeles basin. Minute quantities of sodium phosphate (Na₃PO₄) are present in the brine of Searles Lake.

Plants for converting phosphate rock to superphosphate ($Call_4P_2O_5$) are located at Richmond and Vernon, California. A plant at Permanente produces "Thermo-Phos," a material composed of fused western phosphate rock and California serpentine. In addition, large quantities of superphosphate and prepared phosphate fertilizers are brought in from outside of the state.

POTASH 4

The term "potash" or "actual potash," as used commercially, signifies the equivalent K₂O content of a potassium salt. For statistical purposes, potassium compounds are ordinarily converted to the equivalent amount of K2O. Loosely used, potash implies potassium salts in general.

Potassium in small amounts is a widespread element. It is present in the common rock-forming minerals such as orthoclase (KAlSi₃O₈) and muscovite $(H_2KAl_3(SiO_4)_3)$. The waters of the sea and many saline lakes contain potassium. Both marine and land plants contain recoverable amounts. Potash becomes concentrated in the waste products of some industrial processes and at times has been recovered. The present most important sources are brines and buried deposits of soluble potash minerals.

Soluble salts of potassium are derived from the weathering of rockforming minerals. Carbonic acid, formed by carbon dioxide of the atmosphere, attacks feldspars and produces carbonates. Although the process is probably complex, a representative reaction can be conveniently pictured as follows :

 $KAlSi_3O_8$ (orthoclase) + $H_2CO_3 \rightarrow K_2CO_3$ + kaolinite

Similarly the weathering of sulfides, particularly pyrite, produces soluble sulfates. The weathering of rocks does not produce the quantity of borates and ehlorides found in some waters, and it is thought that they are derived at least in part from volcanic activity. Another source of ehlorides is the sea water that has been trapped in the interstices of marine sediments.

These soluble products dissolve in ground water and find their way to the sea or to undrained basins. Average sea water contains 0.037 percent potassium.⁵ Concentrations in saline lakes may be much greater.

Saline lakes may be arms of the sea that have been cut off such as the prehistorie body of water that occupied the Salton basin, or undrained basins such as the California playas where evaporation approximates the amount of water flowing in. Chemically no two saline lakes are exactly alike.

When a quantity of sea water is evaporated the disolved salts preeipitate approximately in inverse order of their solubilities. Calcium and magnesium carbonates precipitate first. They are followed by ferric oxide, ealeium sulfate, sodium chloride, magnesium sulfate, and magnesium chloride. The remaining liquid, which amounts to 1.6 percent of the orig-

⁴ Ver Planck, W. E., Jr., Potasslum salts in Mineral commodities of California: California Div. Mines Bull. 156, pp. 236-242, 1950. ⁵ Armstrong, E. F., and Miall, L. M., Raw materials from the sea, p. 132, Brooklyn, Chemical Publishing Company, 1936.

inal volume is a bittern containing the very soluble salts of potassium. sodium, and magnesium.⁶

The precipitation of a salt is greatly influenced by temperature, concentration, and the presence of other salts. This fact is particularly pronounced with those salts which remain in the bittern. Not only will there be a different order of precipitation for different brines, but the order may be different for the same brine if conditions vary.⁷

Saline deposits form by the evaporation of saline water in arid regions. They are forming today in the deserts of southeastern California, and similar deposits are known to have formed in the geologic past. The desiccation of a saline lake results in a playa. Most of the California playas are filled almost entirely with mud and are covered with an efflorescent crust of mixed salts, but some playas contain beds of a pure salt or mixed salts. Searles Lake is such a playa.

A single cycle of evaporation would account for the salines found in the playas, but for the thick deposits of relatively pure potash such as those found in New Mexico and Germany, no completely satisfactory explanation has yet been proposed.

Searle Lake, one of the most interesting saline deposits in California, is a playa in which water stands above the surface only after heavy rains. During Pleistocene time it was part of an integrated drainage system that included Owens River, Owens Lake, Searles Lake, Panamint Valley and probably Death Valley.⁸

Today Searles Lake is a vast flat of mud and sand mixed with salts; in its center is a porous crystal body having an area of 13 square miles. The composition of the upper salt body, which averages 70 feet thick, is not uniform. In one bore hole near the center of the lake the following salts were encountered :⁹

| $0-15~{ m ft}$: | Halite (NaCl) |
|----------------------|---|
| 15-20 ft : | Halite, hanksite, (9Na ₂ SO ₄ ·2Na ₂ CO ₃ ·KCl) |
| | and trona (Na ₂ CO ₃ ·NaHCO ₃ ·2H ₂ O) |
| $20-25 \; { m ft}$: | Mostly hanksite |
| 25-40 ft : | Hanksite, halite, trona, and borax (Na ₂ B ₄ O ₇ . |
| 40-75 ft : | Hanksite, halite trong, boray, and glaserite (|

 $(3K_2SO_4 \cdot Na_2SO_4)$ In other holes the same salts are found but in different proportions. A lower salt body, separated from the upper by a layer of impervious mud, was discovered in 1946. The lower salt contains less potash but more carbonate and borate than the upper salt. Neither the crystal bodies nor the brines with which they are saturated contain calcium or magnesium salts.

 $10H_{2}O$)

From the upper brine the American Potash and Chemical Corporation obtains potassium chloride, potassium sulfate, borax, boric acid, soda ash, salt cake, lithium salt, bromine, and bromine salts. Soda ash is also obtained from the lower brine in a separate operation. The successful treatment of the upper brine is a triumph of chemical engineering.¹⁰

⁶ Clarke, F. W., The data of geochemistry: U. S. Geol. Survey Bull. 770, pp. 219-221,

^{1924.}

⁷ Grabau, A. W., Principles of salt deposition, pp 61-75, 1st ed., New York, McGraw-Hill Book Company, Inc., 1920.
⁸ Gale, H. S., Salines in the Owens, Searles, and Panamint basins, southeastern California: U. S. Geol. Survey, Bull. 580, pp. 251-323, 1913.
⁹ Teeple, J. E., The industrial development of Searles Lake brine, pp. 15-16, New York, Chemical Catalor Co. 1929.

York, Chemical Catalog Co., 1929. ¹⁰ Teeple, J. E., The industrial development of Searles Lake brine, p. 18, New York, Chemical Catalog Co., 1929.

1951]

| Salt | Percent by weight | Salt | Percent by weight | | | | |
|---|---|---------------------------------------|---|--|--|--|--|
| NaCl Na ₂ SO ₄ | $16.50 \\ 6.82 \\ 4.82 \\ 4.80 \\ 1.51 \\ 0.155 \\ 0.109 \\ 0.021 \\ 0.020$ | As ₂ O ₃ CaO | 0.019 0.0022 0.0020 0.0018 0.0014 0.0006 34.782 | | | | |

Chemical composition of the upper brine.

Brine from wells sunk in the upper crystal body of the lake, together with recycled mother liquor is concentrated in triple-effect evaporators.¹¹ During the evaporation sodium and lithium salts are precipitated and withdrawn from the evaporators for further treatment. The hot liquor from the evaporators is chilled, and the potassium chloride which precipitates is removed. Further cooling of the filtrate precipitates borax. Much of the potassium chloride is dried and sold for agricultural purposes. Moist potassium chloride is treated with burkeite $(2Na_2SO_4 \cdot Na_2CO_3)$, a salt formed in the main evaporator, to produce potassium sulfate.

Searles Lake is the principal current source of potash in California, but during World War I it was recovered from sea water bittern, kelp, cement mill dust, and industrial waste. Bittern currently produced in the Leslie Salt Company's operations at Newark, Alameda County, contains 1.4 percent KCl at 28° Bé (total solids 28 percent).¹² The potash recovered from cement mill dust by the Riverside Portland Cement Company from 1916 to 1924 contained 11 percent K_2O^{13} Elsewhere in the United States work has been done on the recovery of alumina and potash from alunite, a basic hydrous sulfate of aluminum and potassium containing 11.4 percent K₂O. Deposits of alunite are known in California but potash production from them is not imminent.

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 ¹² Buchen, J. C., Evaporating salt from the world's largest mineral deposit: Min. and Met., vol. 18, no. 367, p. 338, 1937.
 ¹³ Bradley, W. W., Potash: California Min Bur. Bull. 74, p. 112, 1917.

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AGRICULTURAL MINERALS IN CALIFORNIA

BY ROBERT Z. ROLLINS *

OUTLINE OF REPORT

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ABSTRACT

"Agricultural minerals" are mineral substances, mixtures of mineral substances, and mixtures of mineral and organic substances used for promoting or stimulating the growth of plants, increasing the productiveness of plants, improving the quality of crops, or producing any chemical or physical change in the soil, and which contain less than 5 percent of nitrogen, available phosphoric acid, or water-soluble potash. Approximately 500,000 tons of agricultural minerals, valued at \$6,000,000 are used each year in California. Each product must be registered with the State Department of Agriculture, Bureau of Chemistry, before being offered for sale. Each lot or container must show the name and percentage of each constituent of agricultural value claimed to be therein. Samples of materials on the market are drawn and analyzed to determine the conformity of composition with that guaranteed on the label.

INTRODUCTION

California farmers spent approximately \$6,000,000 in 1948 for 500,000 tons of agricultural minerals. During the same period they spent approximately \$42,000,000 for 500,000 tons of commercial fertilizers, and it is estimated that \$20,000,000 was spent for pest control materials.

The importance of agricultural chemicals to California's agriculture is reflected in the provisions of the Agricultural Code pertaining to the registration, labeling, and sale of these products. The law serves to screen out agricultural minerals which are detrimental or injurious to plants when applied as directed, or which are known to be of little or no value for the purpose for which they are intended, or products for which false or misleading claims are made or implied. It forbids misrepresentation in connection with the sale of agricultural minerals, and provides for inspection, sampling, and analysis of materials found offered for sale to determine how the compositions of the materials conform to the guaranteed analyses under which they are sold. The service is selfsupporting by means of registration fees and tomage license taxes.

The Burean of Chemistry is essentially a law-enforcement agency. It does not generally provide recommendations with regard to agricultural problems or advice on use of fertilizing materials. Agricultural research, recommendations, and advisory services are provided by the Agricultural Experiment Station and the Agricultural Extension Serv-

^{*} Assistant Chief, Bureau of Chemistry, State Department of Agriculture.

ice of the University of California, with headquarters in Berkeley, California.

The Agricultural Experiment Station publishes a monthly magazine entitled "California Agriculture" and a number of circulars and bulletins on agricultural matters particularly pertinent to the soils, climates, and crops of this state. A list of available publications may be obtained from the Station. The Extension Service is represented in most counties by a Farm Advisor who provides information and guidance on the agricultural problems of his county. The United States Department of Agriculture distributes Farmers' Bulletins and other publications on agriculture. A list of available publications may be obtained from Division of Publications, Office of Information, U. S. Department of Agriculture, Washington, D. C.

DEFINITIONS OF FERTILIZING MATERIALS

The Fertilizing Materials Article of the Agricultural Code of California applies to any substance or mixture of substances intended to be used for promoting or stimulating the growth of plants, increasing the productiveness of plants, improving the quality of crops, or producing any chemical or physical change in the soil.

The Code provides definitions of five classes of fertilizing materials:

Commercial fertilizers are substances and mixtures of substances containing 5 percent or more of nitrogen, available phosphoric acid, or potash soluble in distilled water, singly, collectively, or in combination, except manures, hays, straws, peat, and leaf mold.

Agricultural minerals are mineral substances, mixtures of mineral substances, and mixtures of mineral and organic substances, containing less than 5 percent in available form of nitrogen, phosphoric acid, or potash, singly, collectively, or in combination, except sand and soil.

Manures are the excreta of domestic animals or domestic fowls when not artificially mixed with any material or materials other than those which have been used for bedding, sanitary, or feeding purposes for said animals or fowls or for the preservation of manure.

Auxiliary plant chemicals are substances such as hormones, auxins, materials for reducing pre-harvest drop of fruit, materials for promoting rooting of cuttings, bacterial inoculants, and similar products intended to be used for influencing plants.

Soil amendments are all other substances, and include hays, straws, peat, leaf mold, and sand.

The term *agricultural mineral* differs from the common term mineral. It includes a few simple mineral species such as gypsum, sulphur, apatite, and calcite. It includes some other simple compounds such as sulphur dioxide, sulphuric acid, and calcium hydroxide. It includes some industrial wastes such as by-product lime and unactivated sewage sludge, and also includes mixtures such as sulphur with limestone, gypsum with grape pomace, and gypsum with peat moss. On the other hand, a few true minerals are not agricultural minerals because, like sylvite (KCl), they contain enough plant food to be classed as commercial fertilizers. Furthermore, some minerals, such as tale and pyrophyllite, are of agricultural importance as dust diluents used for pest control but they are not used as agricultural minerals. No accurate data are available with regard to amounts of minerals used in pest control.

REGISTRATION

Each agricultural mineral must be registered with the Bureau of Chemistry before it is offered for sale in California. Registration may be refused if the proposed composition indicates that the material is injurious to plants or if it is of little or no value for the purpose for which it is intended. The proposed labeling is also examined, and registration may be refused if false or misleading claims are made or implied. Registration thus serves as a screen to eliminate worthless products or proposed misrepresentations before the material is offered for sale.

The registration license fee of \$50 permits registration of any number of products under the same firm name, and supplemental applications for registration of additional products may be submitted at any time Registration is issued on a fiscal-year basis, and must be renewed each year if sale of the product is to be continued.

| Fiscal year | Number of registrants | Fiscal year | Number of registrants |
|-------------|--------------------------|-------------|--------------------------|
| 924-25 | *36 | 1937-38 | 66 |
| 925-26 | *40 | 1938-39 | 72 |
| 926-27 | *41 | 1939-40 | 72 |
| 927-28 | *38 | 1940-41 | 71 |
| 928-29 | 51 | 1941-42 | 71 |
| 929-30 | 47 | 1942-43 | 63 |
| 930-31 | *48 | 1943-44 | 67 |
| 931-32 | *41 | 1944-45 | 89 |
| 932-33 | 43 | 1945-46 | 112 |
| 933-34 | 42 | 1946-47 | 148 |
| 934-35 | 55 | 1947-48 | 165 |
| 935-36 | 49 | 1948-49 | 165 |
| 936-37 | 51 | | |

Table 1. Number of agricultural minerals registrants.

* Registered by December 31 for the fiscal year.

The number of registrant firms has increased in recent years as shown in table 1.

Table 2 shows the number of each type of agricultural mineral registered by March 1, 1950, for the fiscal year 1949-50.

Table 2. Agricultural minerals registered by March 1, 1950,for the fiscal year 1949-50.

| Type of product | Number of products | Type of product | Number of products |
|---------------------------|-----------------------|-------------------------|-----------------------|
| Aluminum compounds | 13 | Iron compounds | 15 |
| Boron compounds | 7 | Magnesium compounds | 6 |
| Caleium carbonate | 51 | Manganese compounds | 10 |
| Calcium bydroxide | 27 | Miscellaneous materials | 23 |
| Calcium oxide | 7 | Mixed materials | 68 |
| Caleium phosphate | -1 | Sewage products | 27 |
| Calcium polysulphide | 16 | Soil sulphur | 52 |
| Caleium sulphate (gypsum) | 91 | Sulphurie acid | 25 |
| Copper compounds | 3 | Zine compounds | 11 |
| Diatomite | 2 | _ | |
| Dolomite | 3 | Total | 461 |

LABELING

Each lot or container of agricultural mineral offered for sale in California must bear a label or tag, stating:

(1) The name, if any, under which the material is to be sold. This may be a common name such as "Agricultural Gypsum," a brand name such as "Bluestar Limestone," or a coined term such as "Soilmaker." The name should not be misleading. In general, a brand name registered for one firm is not accepted for registration for another to avoid confusing users.

(2) The name and address of the registrant firm. This should be a complete street address unless the firm is listed in a local telephone directory or business directory.

(3) The place of manufacture or production. The statement of the country of production, for example, "Product of U. S. A.," is accepted as fulfilling this requirement.

(4) A chemical analysis stating the percentages of every constituent of agricultural value claimed to be therein, and the materials from which all of said constitutents are derived. The guaranteed analysis should not be presented in a misleading manner. Occasionally an applicant for registration proposes to show as a guaranteed analysis, a list of equivalents and percentages reported by a commercial chemist for one sample. In general this is not acceptable because the presentation may be misleading to the average user. Such analytical reports commonly include a number of theoretical components such as "SiO₂," "TiO₂," and "Al₂O₃" which are of no significant agricultural value. It is common for such reports to show total calcium expressed as CaO even though the material contains no quicklime nor calcium in any form suitable for correcting soil acidity. Furthermore, elements such as iron, copper, zinc, and manganese may be included in the report but be present in insignificant amounts or in forms not available to plants. In general the guaranteed analysis should be restricted to a statement of the name and percentage of those constitutents known to be of agricultural value.

This information is sometimes printed on a tag fastened to each sack containing the material or it is printed directly on the bag or carton. Much of the gypsite mined and used in the San Joaquin Valley is handled in loose lots. It is hauled in trucks directly from the open pits, where it is scraped up, to the fields upon which it is to be applied. In such cases the tag bearing the necessary information is firmly attached to a stake driven into the load so as to be plainly visible during transit and upon delivery to the user. Some firms have also developed the acceptable practice of including the required information on a form which also includes the invoice and the weighmaster's certificate pertaining to the specific load. The form is delivered to the user with the material.

TONNAGE LICENSE TAX

The law requires each registrant to submit a quarterly statement of sales and to pay a tonnage license tax of 10 cents per ton. This is equivalent to one-half cent on a 100-pound sack of material. The registration fee and the tonnage license tax render administration of the law self-supporting.

SAMPLING

Official samples are drawn from agricultural minerals found offered for sale in the state. Section 1037 of the Agricultural Code provides that if the material is packaged in containers of less than 10 pounds, one package of the material may be taken as a sample to represent the lot of which it is a part. When material is packaged in containers of ten pounds or more, each official sample consists of at least one pound of material taken in the following manner:

(A) Packaged dry materials. (1) Use a sampler that removes a core diagonally from end to end of the bag. (2) Take cores from all bags if 20 or fewer are present. If 21 to 200 bags are present, take 20 cores from as many bags. If more than 200 bags are present take cores from 20 bags plus 1 bag for each additional ton in excess of 10 tons. (3) Thoroughly mix portions on a clean rubber sheet, oil cloth, or paper, and reduce by quartering to quantity of sample required; sample splitter may be used to quarter. (4) Place opposite quarters in one sample container, remainder in another for duplicate.

(B) Dry materials in bulk lots. (1) Scrape outer surface aside before inserting sampler. (2) Take at least 20 approximately equal cores each from fairly evenly distributed parts of the quantity. If more than 10 tons are contained in a lot take two cores for each additional ton. Portions may be taken with a trowel when the material contains large lumps or when for other reason it is not possible to use a sampler.
(3) Break any lumps, mix, quarter, and place in sample containers as provided in paragraph (A).

(C) Liquid materials packaged in drums or barrels. (1) Use a sampler that will remove a cross section from top to bottom of the container. From each package entered place one sampler-full in each sample container. (2) Enter all containers if fewer than 3; at least 3 if fewer than 10; and 5 if 10 or more are present.

(D) Liquid materials in large containers. To sample a liquid fertilizing material which is packaged in storage tanks, railway tank cars, or similar containers, a sample jar may be lowered into the material and allowed to fill. If this is not possible, the sample jar may be filled from faucet after sufficient material has flowed through faucet to clear connecting line.

The official sample is sealed before removal from the premises where it was drawn. The duplicate portion is sealed and left with the party whose stock was sampled or on the premises where it was drawn.

The number of samples handled each year depends somewhat upon the amount being sold and the number of lots encountered by inspectors. The sampling activities are also adapted according to the findings with certain types of material or certain firms. The record of sampling is presented in table 3.

EXAMINATION OF SAMPLES

Official samples are sent to the main laboratory at Sacramento where they are examined and analyzed to determine if the materials conform to the guaranteed analyses and to any other claims made for their composition. In general most of the examinations are limited to chemical analysis and, in some cases, determination of fineness. Many of the analytical methods used by the Bureau are derived from the "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists." Special procedures are necessary in some eases to avoid interference by accompanying constituents, and from time to time chemists in the Bureau's laboratory contribute new methods to the technical literature of analytical chemistry.

The Bureau of Chemistry does not engage in general analytical work for individuals. This type of service is available from commercial laboratories located throughout the state. According to law a user of a fertilizing material may submit to the Bureau a sample of a material to which the law applies and request analysis to establish the conformity or noneonformity of the sample to the guarantee under which the material is sold or to be sold. The fee for a user's sample is \$2 per constituent determined. However, users seldom avail themselves of this privilege and prefer to have an official sample drawn by the Bureau because no fee is charged for official sampling.

REPORTS OF FINDINGS

A report of the findings is mailed to the registrant of the material and to any dealer, purchaser, or user who may be interested in the particular lot represented by the sample. The results of examinations are compiled each calendar year in a publication which is distributed to anyone free of charge.

| | | Gypsum | Sulphur | Misc. | Total | Deficient | Mis- branded |
|------|-----|--------|---------|-------|-------|-----------|-----------------|
| 1924 | 17 | 7 | 0 | 11 | 35 | 7 | 0 |
| 1925 | 42 | 11 | Õ | 12 | 65 | 11 | 11 |
| 1926 | 18 | 12 | 1 | 4 | 35 | 3 | 9 |
| 1927 | 28 | 21 | 11 | 26 | 86 | 17 | 11 |
| 1928 | 39 | 12 | 9 | 23 | 83 | 15 | 17 |
| 1929 | 50 | 23 | 9 | 22 | 104 | 10 | 19 |
| 1930 | 33 | 9 | 11 | 18 | 71 | 3 | 4 |
| 1931 | 14 | 10 | 6 | 19 | 49 | 8 | 14 |
| 1932 | 25 | 14 | 8 | 17 | 64 | 6 | 13 |
| 1933 | 19 | 13 | 3 | 16 | 51 | 13 | 16 |
| 1934 | 24 | 33 | 11 | 16 | 84 | 15 | 28 |
| 1935 | 22 | 28 | 14 | 23 | 87 | 20 | 31 |
| 1936 | 22 | 20 | 8 | 15 | 65 | 11 | 10 |
| 1937 | 16 | 27 | 14 | 29 | 86 | 25 | 16 |
| 1938 | 13 | 32 | 29 | 23 | 97 | 15 | 19 |
| 1939 | 14 | 51 | 21 | 25 | 111 | 23 | 19 |
| 1940 | 24 | 79 | 22 | 46 | 171 | 47 | 49 |
| 1941 | 17 | 137 | 33 | 24 | 211 | 63 | -43 |
| 1942 | 13 | 87 | 29 | 27 | 156 | 25 | 18 |
| 1943 | 11 | -40 | 19 | 24 | 94 | 23 | 11 |
| 1944 | 5 | 220 | 32 | 17 | 274 | 58 | 13 |
| 1945 | 149 | 96 | 28 | 28 | 301 | 106 | 25 |
| 1946 | 89 | 181 | 26 | 31 | 327 | 59 | 25 |
| 1947 | 60 | 288 | 26 | 65 | 439 | 85 | 72 |
| 1948 | 32 | 180 | 23 | 100 | 335 | 85 | 39 |
| 1949 | 16 | 149 | 34 | 64 | 263 | 49 | 16 |

Table 3. Official samples of agricultural minerals.

* "Limestone" includes marl, hydrated lime, and quicklime.

| C dan dan susan | | Total tons | | | |
|-----------------|----------|------------|----------|---------|------------|
| Calendar year | March 31 | June 30 | Sept. 30 | Dec. 31 | Total tons |
| 1923 | | | | 10,903 | 10,903 |
| 1924 | 11,943 | 6,584 | 7,337 | 18,377 | 44,241 |
| 1925 | 11,411 | 7,276 | 9,886 | 22,161 | 50,734 |
| 1926 | 18,881 | 8,977 | 9,696 | 14,563 | 52,117 |
| 1927 | 18,549 | 11,428 | 11,348 | 18,889 | 60,214 |
| 1928 | 18,724 | 11,906 | 12,832 | 20,546 | 64,008 |
| 1929 | 17,365 | 12,246 | 13,166 | 20,688 | 63,465 |
| 1930 | 13,911 | 11,802 | 11,906 | 16,561 | 54,180 |
| 1931 | 9,604 | 7,284 | 5,597 | 9,568 | 32,053 |
| 1932 | 8,768 | 3,792 | 2,143 | 3,876 | 18,579 |
| 1933 | 3,904 | 3,328 | 4,244 | 8,770 | 20,246 |
| 1934 | 9,572 | 5,808 | 7,968 | 18,502 | 41,850 |
| 1935 | 13,251 | 10,705 | 7,103 | 15,235 | 46,294 |
| 1936 | 10,390 | 8,169 | 10,115 | 24,646 | 53,320 |
| 1937 | 8,671 | 11,629 | 11,524 | 20,979 | 52,803 |
| 1938 | 11,919 | 11,695 | 6,773 | 18,025 | 48,412 |
| 1939 | 15,261 | 9,185 | 8,947 | 33,218 | 66,611 |
| 1940 | 26,557 | 20,868 | 19,745 | 41,896 | 109,066 |
| 1941 | 28,682 | 30,405 | 26,674 | 73,369 | 159,130 |
| 1942 | 56,041 | 30,176 | 45,120 | 103,457 | 234,794 |
| 1943 | 62,230 | 54,923 | 86,753 | 176,920 | 380,826 |
| 1944 | 171,467 | 79,659 | 88,399 | 177,122 | 516,647 |
| 1945 | 141,862 | 77,623 | 73,991 | 185,534 | 479,010 |
| 1946 | 167,553 | 75,591 | 70,696 | 226,771 | 540,611 |
| 1947 | 234,208 | 75,176 | 77,513 | 218,625 | 605,522 |
| 1948 | 210,755 | 71,035 | 66,529 | 148,564 | 496,883 |
| 1949 | 166,412 | 64,928 | 62,238 | 128,906 | 422,484 |

Table 4. Total agricultural minerals tonnage by quarters.

If the sample conforms to the guaranteed analysis, and everything else appears to comply with the requirements of law, the report of analysis is issued with the decision "Passed." If analysis shows that the sample is short by more than 5 percent of the amount guaranteed (this is the tolerance provided by law), the report is issued with the decision "Deficient." If the labeling of the material sampled fails to comply with some requirements of law, the report bears the decision "Misbranded." The record of findings is included in table 3.

If the examination indicates that the material was seriously deficient, the registrant generally makes prompt settlement with the user and notifies the Bureau what compensation has been made. If the deficient material or portions of it are still on the market when the report is issued, the registrant may have the lot returned to him for reworking so it will meet the guaranteed analysis. In some cases, the registrant prefers to re-label the deficient lot with another statement of ingredients in conformity with the findings. Repeated deficiencies may lead to cancellation of registration.

TONNAGE DATA

The tonnages of agricultural minerals reported by registrants for each quarter of the year are shown in table 4. It will be observed that the total tonnage has increased tremendously during recent years and that there is a distinct seasonal usage. Most of the tonnage is used in the winter

| Total | 44,241 | 52.117 52.117 | 60,214 | 64,008 | 54 180 | 32.053 | 18,579 | 20,246 | 41,850 | 46,294 | 53, 320 | 52,803 | 48,412 | 66,611 | 109,066 | 159, 130 | 234,794 | 380,826 | 516, 647 | 479,010 | 540,611 | 605,522 | 496,883 | 422,484 |
|---------------------------------------|--|------------------|--------|---|--|--------|--------|--|----------------------------|--|---|--|--|---|---------|----------|---------|---------|----------|---------|---------|---------|---------|---------|
| Correction by audit | | | | | 8 8 9 1 9 1 8 7 8 7 8 8 | | | 516 | 1,391 | 3,119 | 1,916 | 3,0.43 | 1,653 | 1,510 | 6,024 | 3,830 | 1,108 | 5,484 | 18,278 | 1,984 | 23 | 10,725 | 587 | |
| Not segregated by registrant | 4,358 | 2.275 | 5,295 | 2,503 6 000 | 6.578 | 4,426 | 2,054 | 1,031 | 4,333 | 4,507 | 4,988 | 3,122 | 9,286 | 128 | | 498 | 837 | 1,018 | 1,388 | 640 | 84 | | 1,243 | 116 |
| Miscel- laneous** | 1,848 | 3,713 4,821 | 5,893 | 7,534 | 210:0 | 3,435 | 1,547 | 320 | 1,728 | 1,710 | 1,275 | 1,014 | 941 | 2,941 | 8,677 | 13,009 | 455 | 512 | 1,579 | 1,248 | 7,693 | 19,469 | 20,759 | 13,318 |
| Soil Sulphur | 810 | 493 | 400 | 1 200 | 1.327 | 654 | 276 | 573 | 1,677 | 2,163 | 2,496 | 2,517 | 3,635 | 4,562 | 5,193 | 7,535 | 7,720 | 18,364 | 36,974 | 24,056 | 26,126 | 23,519 | 20,304 | 16,988 |
| Sewage studge | | | | | | | | | | 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | 5 7 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 | 1 0 7 8 1 8 1 8 1 8 1 8 1 8 | | | | 22,549 | 21,286 | 29,102 | 29,597 | 25,509 | 23,199 | 28,920 | 24,816 |
| Phosphate rock | 6 8 7 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 | | 26 | 193 | | | | L 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | 1 1 3 3 4 4 | 8 6 8 8 8 8 8 8 8 8 8 8 8 8 8 | | | 623 | 1 | 375 | , 510 | 563 | 344 | 139 | 44 | 81 | | 364 | 573 |
| Mixed goods | 2,188 | 8,906 | 9,553 | 8,012 | 3.188 | 1,181 | 544 | 598 | 954 | 1,634 | 2,009 | 3,068 | 4,352 | 5,358 | 2,424 | 2,490 | 2,853 | 4,396 | 4,374 | 5,845 | 9,025 | 4,386 | 3,581 | 4,816 |
| Metallic salts | 1 1 1 1 1 8 7 8 7 8 9 | | | | | | | 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | | 1 1 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 | | 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 | | 1 1 1 1 1 1 1 1 | 136 | 180 | 222 | 122 | 217 | 146 | 860 | 1,033 | 1,392 | 1,281 |
| Lime- stone* | 19,630 | 16,600 | 19,715 | 23,001 | 13.687 | 11,884 | 6,717 | 9,008 | 11,506 | 4,223 | 3,881 | 3,017 | 2,136 | 1,705 | 1,411 | 1,620 | 1,222 | 4,128 | 3,338 | 26,521 | 29,546 | 18,533 | 12,697 | 10,495 |
| Lime* | 11,321 | 7,876 | 9,076 | 8,003 19 269 | 9.954 | 4,890 | 3,031 | 4,582 | 12,347 | 12,151 | 19,427 | 12,804 | 8,206 | 7,529 | 7,631 | 7,154 | 11,409 | 24,192 | 26,084 | 21,821 | 27,378 | 14,390 | 12,057 | 11,741 |
| Gypsun | 4,086 | 11,049 | 10,185 | 14,120 | 11.449 | 5,583 | 4,410 | 3,618 | 7,914 | 16,787 | 17,328 | 24,218 | 17,580 | 42,878 | 77,195 | 122,304 | 185,856 | 300,980 | 395,174 | 367,108 | 414,286 | 490,268 | 394,979 | 338,340 |
| Year | 1924 | 1926 | 1927 | 1928 | 1930 | 1931 | 1932 | 1933 | 1934 | 1935 | 1936 | 1937 | 1938 | 1939 | 1940 | 1941 | 1942 | 1943 | 1944 | 1945 | 1946 | 1947 | 1948 | 1949 |

Table 5. Tonnages of agricultural minerals sold in California.

MINERALS USEFUL TO CALIFORNIA AGRICULTURE [Bull.

* "Lime" includes quicklime, air-slaked lime, hydrated lime, and by-product lime. "Limestone" includes limestone rock, shells, and marl. ** The private business of the registrants has been sufeguarded by segregating only those items reported by three or more firms.

months. This is partly due to the fact that agricultural minerals are generally applied when the soil is being prepared for planting. Relatively small amounts are used to side-dress growing crops. Furthermore much of the tonnage of the San Joaquin gypsite deposits is trucked during winter months when trucks are more readily available.

A segregation of the total annual tonnages according to type of material is presented in table 5. It will be observed that approximately threequarters of the total tonnage represents gypsum. The predominance of this particular agricultural mineral is due in part to the fact that many surface deposits of gypsum are along the western edge of the San Joaquin Valley within trucking distance of large agricultural areas where use of the cheap, and readily available gypsum has been found profitable. The tonnages of "gypsum" in table 5 refer to the tonnages of material sold as an agricultural mineral. Part of the tonnage refers to high-grade material containing $CaSO_4 \cdot 2H_2O$, 90 percent or higher, and part of the tonnage refers to gypsite containing CaSO₄·2H₂O, 70 percent, or lower. The true gypsum, $CaSO_4 \cdot 2H_2O$, equivalents of the tonnage data are not known but in recent years approximately three-quarters of the tonnage has been San Joaquin gypsite containing about 70 percent and one-quarter has been high-grade material containing 90 percent or more. Similarly, the ton-nages of "lime," "limestone," and "sulphur" refer to gross tons sold and not to tons of equivalent pure chemicals. Representative analyses reported by the Bureau each year provide a picture of the grades or percentages commonly marketed.

Although the tonnage of metallic salts reported does not appear to be large, it has increased significantly during the last few years. This figure includes the tonnages of aluminum sulphate, copper sulphate, iron sulphate, manganese sulphate, magnesium sulphate, and zine sulphate. The increased usage reflects the current general interest in micronutrients.

MICRONUTRIENT PROBLEM

The three common plant foods supplied by commercial fertilizers are nitrogen, phosphorus, and potassium. These three elements are the ones most commonly deficient in the agricultural soils throughout the world, and therefore the ones most commonly applied in the form of fertilizing materials. A number of other elements are of equal importance in plant nutrition, but an adequate supply of them is usually present in most soils and additions in the form of fertilizing materials are generally not necessary.

Soils differ greatly in different parts of the country. There appears to be a general shortage of boron in the soils of New Jersey, for example; and the sandy, highly-leached soils of Florida are deficient in copper, zine, manganese, and other elements. Few soils in California have been reported to be deficient in any of these micronutrients, and general application of them to soils in this state seems not justified and possibly injurious. Boron is known to be deficient in a few areas in the state and to be present in detrimental excess in other areas. Symptoms of manganese deficiency have been observed in a few orchards. Excess amounts of molybdenum in the soils of some areas have been picked up by forage plants and injured livestock feeding on the plants.

In many places in the state, symptoms of zinc deficiency have been observed on orchard trees. The symptoms are called "little leaf" on peach trees, plum trees, and grape vines, and "mottle leaf" on citrus trees. In some cases, the soils appear to contain an abundant supply of zinc, but it is apparently not in a form that is available to the trees growing in the soil. Application of additional supplies of zinc compounds to the soil are generally ineffective, and the element is applied directly to the foliage in the form of a spray.

The problem is further complicated by the observation that annual plants may thrive in soils in which trees exhibit serious deficiency symptoms. It is evident that some "deficiency" symptoms are due to unavailability of the element to the plant rather than a true shortage of the element in the soil.

Not infrequently a firm will attempt to register as an agricultural mineral a material such as elay, mine tailings, lignite, or a deposit from an old lake bed. The applicant will submit as the proposed guaranteed analysis a chemist's report showing small amounts of most of the common elements found in ordinary soils. Such a guaranteed analysis is generally not acceptable because it infers that the elements guaranteed are of agricultural value, although the small amounts present or the unavailable forms in which they are present indicates that they are of no significant value when applied to soil.

SPECIFIC MATERIALS

Aluminum Sulphate. Aluminum sulphate is not widely used by farmers as an agricultural mineral, but some is regularly sold in garden and nursery trade for acidifying soil around hydrangeas, rhododendrons, azalias, and camellias. The customary formula for the hydrated crystalline form is $Al_2(SO_4)_3 \cdot 18H_2O$. According to this chemical formula, the pure crystalline compound contains aluminum expressed as metallic 8.09 percent. Analyses of official samples generally show aluminum expressed as metallic approximately 8.00 percent to 9.50 percent, indieating that the commercial material is partially dehydrated.

Tonnages sold in California in recent years have been reported as follows:

| Calendar year | Tons of Aluminum Sulphate |
|---------------|---------------------------|
| 1946 | 34 |
| 1947 | 31 |
| 1948 | 27 |
| 1949 | 32 |

Alunite. Alunite is a basic hydrous sulphate of potassium and aluminum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$. The formula indicates that the pure mineral contains potash, K_2O , 11.37 percent, and aluminum expressed as anhydrous aluminum sulphate 41.30 percent. The potash is not soluble in water, but it may be rendered soluble by roasting. A sample of processed alunite analyzed in 1947 was found to contain watersoluble potash 9.20 percent and aluminum expressed as anhydrous aluminum sulphate 24.90 percent. A sample analyzed in 1948 contained 9.34 percent and 35.28 percent respectively. Strictly speaking, such a processed alunite is not an agricultural mineral but a commercial fertilizer according to the definitions of California law, because it contains 5 percent or more of water-soluble potash.

Occasionally processed alunite has been registered for small-package sale in California, but it has never represented any significant tonnage.

Boron Compounds. Symptoms of boron deficiency have been observed on a number of agricultural plants in California and injury from excess of boron in soils and irrigation waters has also been observed. In some states, New Jersey for example, deficiencies are so common and excesses are so rare, that mixed fertilizers generally include about 5 pounds of borax in every ton. Such practice could not be followed in California because it would lead to severe injury to some crops in some areas. The diversity of crops, soils, and weather conditions in California do not permit general recommendations with regard to boron. The Agricultural Experiment Station recommends that extreme caution be used in making any application of boron compounds to the soil. It should be applied only to soils known to be deficient and only in the low dosages needed for correction in the particular area.

In California, deficiency symptoms have been observed on apples in El Dorado and Sonoma Counties, on olives in Butte County, and on celery. Injury from excessive boron has been observed on peaches in the Hollister area and on walnuts in the Davis area.

Unlike other micronutrient elements occasionally needed by plants in California, boron is usually applied to the soil. Apparently it is not fixed in the soil as much as zinc, manganese, and some of the other elements are, and supplies of boron added to the soil appear to be available to plants. Boron deficiency symptoms may therefore be due to a true shortage of boron in the soil, in contrast to deficiency symptoms of some other elements which are often due to a lack of availability of the element already present in the soil.

The boron compound most commonly used as an agricultural mineral is borax, $Na_2B_4O_7 \cdot 10H_2O$, which contains 11.35 percent of elemental boron. When applications are made in California, generally only a few pounds per acre suffice. However, soils differ greatly, and in Sonoma County as much as 10 pounds of borax were applied to the soil around each apple tree in one treated orchard. Approximately 1 pound per tree was applied to olive trees in Butte County. It is not known whether one application is sufficient in all cases or whether subsequent treatments may be necessary.

The tonnages of borax applied to soil in California as an agricultural material have not been large.

| Year | Tons of Borax |
|------|---------------|
| 1946 | 67 |
| 1947 | 202 |
| 1948 | 54 |
| 1949 | 36 |

Borax and other boron compounds are also used for control of certain kinds of weeds, particularly Klamath weed which is a pest of pasture lands in the northern part of the state. Approximately 3 pounds of borax per hundred square feet are applied. No accurate data are available on the total amounts of borax used for this purpose, but it is known to exceed the tonnage reported as an agricultural mineral. For example, 580 tons were reported to have been used for Klamath weed in Tehama County during 1946.

Calcium Carbonate. Liming materials for agricultural use may be ground limestone, mark, or ground shells or they may be derived from air-slaked lime, beet-sugar lime, or other similar industrial by-products. 5-34354 The compound most commonly used is calcium carbonate in the form of limestone or marl. Approximately 51 limestone and marl products are registered for sale in California. The guaranteed percentages of calcium carbonate range from 25 percent to 98 percent.

Large quantities of agricultural limestone are regularly used in north central states to prevent soils from becoming too acid, but comparatively small amounts are used in California where most agricultural soils are alkaline. The tonnages reported in California are shown in table 6. By way of comparison, Illinois uses about 5,000,000 tons and Iowa uses about 3,000,000 tons of agricultural limestone each year.

The fineness of agricultural limestone is a matter of some concern where large amounts are used. The fine particles react more rapidly than the coarse ones. Fine material is desirable where a quick action is desired but coarse material is desirable where a lesser effect over a long period is wanted. In general the materials used in the east are ground to pass a 20-mesh sieve. There are no specific requirements with regard to fineness in California. Any fineness may be sold, but if a certain fineness is guaranteed, the material must meet the guarantee.

| Year | Tons | Year | Tons | Year | Tons |
|--|---|------|---|--|--|
| 1924 1925 1926 1927 1928 1929 1930 1931 1932 | $19,630 \\ 16,644 \\ 16,600 \\ 19,715 \\ 23,001 \\ 18,160 \\ 13,687 \\ 10,884 \\ 6,717 \\ 19,681 \\ 10,100 \\ 10$ | 1933 | $\begin{array}{c} 9,008\\ 11,506\\ 4,223\\ 3,881\\ 3,017\\ 2,136\\ 1,705\\ 1,411\\ 1,620\\ \end{array}$ | 19-12 1943 1944 1945 1946 1947 1948 1949 | $\begin{array}{c} 1,222\\ 4,128\\ 3,338\\ 26,521\\ 29,546\\ 18,533\\ 12,697\\ 10,495\end{array}$ |

Table 6. Tons of agricultural limestone reported in California.

Calcium Hydroxide. Calcium hydroxide, commonly ealled hydrated lime or slaked lime, is used mainly for correction of acid soils which are found in a few agricultural areas in California. Much of the tonnage is derived as waste material from lime kilns. Guarantees of actual calcium hydroxide run from 70 percent to 90 percent.

In addition to this, California agriculture uses a number of "byproduct limes" derived from kiln rejects, sugar-beet refineries, and other industrial processes. The materials are usually mixtures of calcium oxide, calcium hydroxide, and calcium carbonate. The tonnages sold in California are shown in table 7.

In addition to the tonnages sold to users, an unknown amount of by-product lime is given to cooperating growers by sugar-beet refineries. No accurate figures are available, but it is estimated that about 20,000 tons are so distributed each year.

Calcium Phosphate (Phosphate Rock). Phosphate rock is a mixture of fluor-apatite and impurities. No significant deposits have been found in California but large quantities are mined in Idaho and Wyoming, and in Tennessee, South Carolina, and Florida. It is the primary source of practically all the phosphorus used in fertilizing materials. The raw rock is treated with sulphurie aeid, forming superphosphate, to render the phosphorus more readily available to plants. Approximately

| Year | Tons hydrated lime | Tons by-product lime | Year | Tons hydrated lime | Tons by-product lime |
|------|--------------------------|----------------------------|------|--------------------------|----------------------------|
| 1924 | 117 | 11,204 | 1937 | 475 | 12,329 |
| 1925 | 929 | 12,954 | 1938 | 1,649 | 6,557 |
| 1926 | 407 | 7,469 | 1939 | 1,042 | 6,487 |
| 1927 | 481 | 8,595 | 1940 | 1,352 | 6,279 |
| 1928 | 667 | 7,336 | 1941 | 1,090 | 6,064 |
| 1929 | 1,399 | 11,463 | 1942 | 1,044 | 10,365 |
| 1930 | 2,255 | 7,699 | 1943 | 1,628 | 22,564 |
| 1931 | 1,335 | 3,555 | 1944 | 4,586 | 21,498 |
| 1932 | 508 | 2,523 | 1945 | 10,412 | 11,409 |
| 1933 | 234 | 4,348 | 1946 | 6,782 | 20,596 |
| 1934 | 543 | 11,804 | 1947 | 1,182 | 13,208 |
| 1935 | 783 | 11,368 | 1948 | 1,130 | 10,927 |
| 1936 | 2,119 | 17,308 | 1949 | 1,353 | 10,388 |

Table 7. Tons of agricultural hydrated lime and by-product limereported in California.

150,000 tons of phosphate rock were used in the manufacture of the superphosphate applied in California in 1949.

Increasing amounts of the untreated rock are being applied directly to soils in some other states, particularly in Illinois, where it has been found to be profitable on acid or slightly acid soils. It is generally believed to give no profitable return on neutral or alkaline soils, in which soils the phosphorus may not be available to plants. Unlike those in eastern states, few agricultural soils in California are acid and no significant amounts of phosphate rock have been used for direct application in this state. The tonnages reported in California are shown in table 8.

Analyses of phosphate rock sold for direct use are fairly uniform and the following results on a recent sample are typical:

| Available phosphoric acid | 2.7% |
|---------------------------|-------|
| Insoluble phosphoric acid | 29.5% |
| Total phosphoric acid | 32.2% |

Available phosphorie acid in rock phosphate is determined by the official neutral eitrate method adopted by all regulatory agencies. The 2 percent citric acid method used for basic slag is not applicable to phosphate rock, but when it was used on this sample for comparison, 6.2 percent of phosphoric acid was found to be soluble. The fineness of the material was such that \$2.8 percent passed through a 200-mesh screen.

| Year | Tons | Year | Tons | Year | Tons |
|---|-----------------|--|-------------------|--|---|
| 1924 - 1925 - 1926 - 1927 - 1928 - 1929 - 1931 - 1932 - | 97 97 193 | 1933 1934 1935 1936 1937 1938 1939 1940 1941 | 623 375 510 | 1942 1943 1944 1945 1946 1947 1948 1949 | 563 344 139 44 81 364 573 |

Table 8. Tons of untreated phosphate rock reported in California.

Calcium Polysulphide (Lime-Sulphur). Calcium polysulphide is the chief constituent of lime-sulphur solution, which is formed by heating a suspension of calcium hydroxide and elemental sulphur. Limesulphur solution has been commonly used for many years as a dormant spray for control of certain pests on fruit trees and as a dip for control of certain parasites on livestoek. Small amounts of the solution were occasionally used as an agricultural mineral for treatment of soils about 25 years ago, but the amounts were not significant. A general interest in use of sulphur compounds on soils became evident about 3 years ago. No appreciable tonnage of lime-sulphur solutions was reported as an agricultural mineral in 1946, but 2,620 tons were used in 1947, 3,728 tons in 1948, and 2,787 tons in 1949.

Lime-sulphur solutions are uniformly prepared to contain calcium polysulphide 29 percent, equivalent to combined calcium about 6 percent, and combined sulphur about 23 percent. The solutions are strongly alkaline, about pH 12.5. However, when the diluted solution is applied to the soil, it decomposes and the excess elemental sulphur is slowly oxidized to sulphuric acid.

One gallon of lime-sulphur solution contains about 2.5 pounds of total sulphur; about 0.6 pound of this ends up as gypsum, which is essentially neutral in reaction, and 1.9 pounds is available for neutralization of soil alkalinity. Therefore, addition of 1 gallon of lime-sulphur solution to soil should give approximately the same final result as adding 3.3 pounds of gypsum and 1.9 pounds of elemental sulphur.

The solutions are generally applied by being metered into the irrigation water. Up to 10 gallons per acre are used when irrigating growing crops and application is repeated several times a year. Where used as a pre-planting treatment on bare ground, 20 or 30 gallons per acre are applied in one irrigation. Little information on the practice has appeared in the scientific literature and apparently such usage is not common in other states.

Clay. From time to time, some interest is shown in the possibility of marketing a clay such as bentonite or montmorillonite for agricultural use. Chemical analysis indicates that most such materials do not contain any significant amount of plant foods nor any other ehemical components of known agricultural value. Some clays from recent deposits contain an appreciable amount of organic matter, and are light and fluffy materials.

No experimental data appear to have been published demonstrating any significant effect from addition of clays to common soils. It is conceivable that they might have a beneficial effect on the physical nature of some coarse soils, improving their water-holding capacity, baseexchange properties, or retention of plant foods, but this has not yet been proven by laboratory or field tests.

Copper Sulphate. Some plants suffer from a deficiency of eopper. This has been noted in California with apple, pear. prune, and citrus trees, but it has not been observed in annual plants in this state. The disturbance in both deciduous trees and citrus trees is commonly called "dieback" or "exanthema". It is not wholly clear whether the deficiency is related to an actual shortage of copper in the soil or to a fixation of copper in some form in which it is not available to plants. Copper sprays and dusts are widely used in California agriculture for control of fungi on many kinds of plants. A special survey was made in 1942 to estimate the amount of the copper compounds used as fungicides in California. The data indicated that approximately 2,000 tons of copper expressed as metallic were applied each year. It is possible that such large, widespread, and regular applications of copper fungicides may be supplying an incidental correction of incipient copper deficiencies which would otherwise be manifested. There is no evidence that this is actually the case, but it is interesting to note that copper does serve a dual role in nutrition and protection of plants.

Copper fungicides are of course applied directly to the plants. Copper compounds for alleviation of a nutritional deficiency are applied (1) as a spray to the plant, (2) by injection into the trunk or limbs of the tree, or (3) sometimes by application to the soil.

Accurate data are not available with regard to the tonnage of copper used each year as a fungicide. The amounts used specifically as a plant nutrient are not large, as shown by the agricultural minerals tonnages reported.

| Year | Tons of | Copper Sulphate |
|------|---------|-----------------|
| 1946 | | 8 |
| 1947 | | 64 |
| 1948 | | 272 |
| 1949 | | 118 |

Diatomite. Diatomite is also called diatomaccous earth, infusorial earth, siliceous earth, fossil flour, and kieselguhr. It is a deposit of the skeletons of microscopic diatoms and is chiefly silicon dioxide. Deposits are found in many places in California, and large amounts are used in industrial filtrations and in heat insulation.

Some interest has been shown in the possible use of diatomite as an agricultural mineral. It does not contain any significant amount of any plant food and there is no evidence that the material is of value because of its chemical constituents. However, it is a very light, porous, and powdery material and it has been used to modify the texture of heavy, compact soils in somewhat the same manner as straw, peat, or sand is sometimes used. A small amount was first reported as an agricultural mineral in 1947, 160 tons were reported in 1948, and 636 in 1949. Some of the material may be used by manufacturers of mixed fertilizers as a filler or conditioner, but no data are available on tonnages so used.

Flue Dust. The dust formed in the manufacture of cement is usually trapped by a Cottrell precipitator or similar device installed in the flue. In some operations the recovered flue dust is fed back into the feed system, but it may be sacked and sold as a fertilizing material. One such product on the market is guaranteed :

| Calicum carbonate equivalent | 50% |
|------------------------------|-----|
| Magnesium carbonate | 1% |
| Potash in water-soluble form | 2% |

Iron Sulphate. A trace of iron is essential to the development of plants, but iron is widespread in most soils and addition of iron compounds to the soil as a plant nutrient is rarely justified. Under some eircumstances, trees develop a yellow condition called chlorosis which appears to be due to a deficiency of iron, although the trees are growing in soils which contain normal quantities of iron. This type of disturbance

occurs in a number of areas throughout California. It is commonly attributed to an excess of lime in the soil, but other factors may also be involved.

"Soils containing an excess of lime usually contain also an abundance of iron but in a form insufficiently available to many plants. It has proven generally impracticable, thus far, to make the iron in the soil available, or to increase the amount of available iron present by the surface addition of fertilizers containing iron. The presence of excess lime in the soil quickly renders applied iron insoluble and unavailable. The only practicable, immediate cure for lime-induced chlorosis is to apply iron in suitable form and amount directly to the plant."¹

Subsequent investigations by the station have shown that application of iron sulphate to the soil has been successful on roses and shallowrooted shrubs in a few areas. Sprays applied directly to the foliage have given temporary correction in some cases, but in general, injection of iron salts directly into the trunk or limbs of the trees has been necessary to secure correction for several seasons.

The problem is somewhat complicated by the common observation that some species of trees are affected while others growing in the same soil develop normally. Annual crops have not exhibited any symptoms of iron deficiency in any area in California. Thus a cover crop in an orchard may thrive while the trees it surrounds suffer from inability to obtain iron from the same soil.

For some unknown reason persons not familiar with the available information frequently believe that addition of iron compounds to agricultural soils is exceedingly important, and many attempts have been made to market low grade iron ores for agricultural use. Registration cannot be issued until adequate information is available to demonstrate that such ores have agricultural value.

Only small amounts of iron sulphate were sold as agricultural mineral until 3-years ago when sales increased sharply. Tonnages reported during the past 4 years are :

| Year Tons of | Iron Sulphate |
|--------------|---------------|
| 1946 | 133 |
| 1947 | 145 |
| 1948 | 235 |
| 1949 | 196 |

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Kelp. The plant food content of kelp is similar to that of manure. It contains approximately nitrogen 1 percent, available phosphoric acid 1 percent, and potash 2 percent. When supplies of potassium salts from Germany were cut off in 1918, approximately 400,000 tons of this seaweed were harvested from the sea and burned to secure potash. This was an expensive procedure, and it ceased as soon as normal mineral supplies were again available.

Since then development of large domestic supplies of potash minerals has rendered kelp an uneconomical source of this fertilizer ingredient. However, about 60,000 tons of kelp are harvested annually in California for production of agar, ice cream stiffener, medicinal products, and feed for livestock. If kelp sold for agricultural use contains 5 percent or more of the three primary plant foods, it is a commercial fertilizer; if less than 5 percent it is probably a soil amendment according to the definitions in the law.

¹ The treatment of lime-induced chlorosis with iron salts: California Agr. Exp. Station Circ. 321, 1931.

Magnesium Compounds. Application of magnesium compounds such as magnesium sulphate or magnesium oxide to agricultural soil has been found of value in eastern states, but no considerable tonnage is used in this state. "Magnesium deficiency has been reported in widely scattered places over the world, but not, so far, in California."²

Dolomitic limestone has been used in this state. It appears to be suitable for its neutralizing value, as any limestone would be, but there have been no reports that it is of any particular value because of its magnesium content.

Manganese Compounds. A deficiency of manganese has been noted on apricot, peach, walnut, and citrus trees in California. The deficiency is sometimes corrected by sprays and sometimes by injection of manganese sulphate directly into the trunk of the trees. Applications to the soil in California are apparently becoming more common according to the tomage data submitted for manganese sulphate sold as an agricultural mineral.

| Year | · Tons of Ma | nganese Sulphate |
|------|--------------|------------------|
| 1946 | | 250 |
| 1947 | | 345 |
| 1948 | | 604 |
| 1949 | | 344 |

Potassium permanganate has been used as a source of soluble manganese in some investigations reported in the literature, but manganese sulphate seems to be the only manganese compound commonly used in California for this purpose. Pure anhydrous manganese sulphate contains manganese expressed as metallic 36.38 percent. The commercial grade material is usually a mixture of hydrated crystalline forms containing four or five molecules of water of hydration. Some are guaranteed to contain manganese expressed as metallic 23 percent and some 29 percent.

Peat. Peat is partially decomposed moss, tules, sedges, or similar organic materials. According to California law, it is a soil amendment and not an agricultural mineral but it is included here because of its similarity with other materials discussed.

Peat is not generally used in commercial agriculture in California. although large amounts are used by florists, nurserymen, and gardeners in cultivation of ornamental plants. It does not contain any significant amount of plant foods, but it is used solely to improve the physical structure of soils. Some peats contain 1 or 2 percent of nitrogen, but it may not be in a form readily available to plants.

Sphagnum peat moss is brought into California from eastern United States, western Canada, and from Europe. Hypnum peat moss has been marketed from a deposit in Modoc County. Sedge and tule peat is marketed from deposits in the Stockton delta region, Los Angeles County, Orange County, San Bernardino County, and Santa Cruz County. No accurate figures are available on the tonnages used in the state.

Perlite. Perlite is a volcanic glass or obsidian which expands or pops when heated to form a light bulky mass of fine spherical particles. It is an aluminum silicate and contains no plant foods. Whatever agricultural value it may possess is due to its physical nature, as discussed under pumice.

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² Proebsting, E. L., Fertilizers and cover crops for California deciduous orchards: California Agr. Exp. Station Circ. 354, p. 5, 1943.

Pumice. Registration is occasoinally secured to sell pumice as an agricultural mineral. It is light and porous and may be of some value in improving the structure of heavy, impervious soils in gardens or in preparation of potting mixtures in greenhouse culture.

Many soils contain adequate plant foods but they are so hard and compact that tillage is difficult and irrigation water does not penetrate well. Various materials are used to lighten the soil so it will crumble or to increase the porosity so water and plant roots are not unduly confined. This may be done with light, bulky organic materials such as peat, straw, sawdust, and shavings or with porous or granular mineral substances such as sand, pumice, perlite, and vermiculite.

Pumice contains no plant foods, and whatever agricultural value it may have is due to its physical structure. The agricultural value of pumice and similar materials is not sufficiently great in ordinary crop production to justify the cost of production, preparation, packaging, and transportation. Some small-package sales have been made for use in gardens, on potted plants, and in nurseries and greenhouses where the material can sell for a higher price than would be economical in ordinary farming.

The chemical composition of pumice and similar materials is of no significance in their agricultural use, and in fact it may be misleading unless fully understood. Occasionally someone interested in marketing such a material for agricultural use submits a sample to a commercial chemist for analysis. The report commonly shows some 10 or 20 elements listed as the oxides and present in a fraction of 1 percent or in traces estimated spectroscopically and too small for chemical determination. Such a list may impress persons not familiar with the fact that any sample of rock or soil contains a similar proportion of impurities. Use of such a chemical analysis in advertising or labeling the material may constitute misrepresentation if it engenders the belief that the material provides a significant and valuable source of micro-nutrients for plants.

Sales of pumice as an agricultural mineral never have exceeded a few tons in occasional years, and the amount sold for this purpose has not been enough to warrant continuance of registration by any one firm for more than two years.

Sewage Sludge. Sewage sludge is a valuable source of plant foods and large quantities are utilized as a fertilizing material in California. Ordinary sewage sludge, which is obtained by simple drying of sewage, contains approximately nitrogen 2 percent and phosphoric acid 1 percent. Activated sewage sludge, which is obtained by aeration and other treatment of sewage, contains approximately nitrogen 5 percent and phosphoric acid 3 percent. Neither type of material contains any significant amount of potash. According to the definitions of California law, ordinary sewage sludge is an agricultural mineral because it contains less than 5 percent plant foods, and activated sewage sludge is a commercial fertilizer.

Sales of both materials in California during the past 10 years are shown in table 9.

The California State Department of Public Health has adopted regulations concerning use of raw sewage and raw unactivated sewage sludge as fertilizing materials to avoid contamination of food crops.

| Year | Ordinary sewago sludge | Activated sewage sludge | Year | Ordinary sewage sludge | Activated sewage sludge |
|---|------------------------------|---|--|--|---|
| 1939 1940 1941 1942 1943 1944 | 22,549 21,286 29,102 | $\begin{array}{c} 1,181\\ 2,252\\ 3,771\\ 4,248\\ 2,743\\ 3,135\end{array}$ | 1945 1916 1947 1947 1948 1949 | $\begin{array}{c} 29,597\\ 25,509\\ 23,199\\ 28,920\\ 24,816\end{array}$ | 1,467 2,765 5,398 7,220 8,280 |

Table 9. Tons of sewage sludge reported in California.

Properly treated activated sewage sludge does not present a health hazard.

Shale. Occasionally some interest is shown in marketing an expanded sintered shale for nursery and garden use. The material is porous and might serve the same purpose as vermiculite, perlite, or punice as a coarse, absorbent medium for growing plants, or for improving the porosity of heavy clay soils. It contains no plant foods and whatever value it has for growing plants is due to its physical nature.

Sulphur. Sulphur is an important element in California agriculture. Large amounts of elemental sulphur and of sulphur compounds are applied to soils in this state. When elemental sulphur is added to soil, it is converted by bacterial action into sulphuric acid. For this reason, elemental sulphur is used to treat alkaline soils which contain a detrimental excess of sodium carbonate. The ultimate action of the sulphur converts the sodium earbonate (black alkali) into sodium sulphate (white alkali) which is more readily removed by leaching.

Large amounts of sulphur are also used to supply the element for plant nutrition. The California Agricultural Experiment Station states that legumes such as bur clover and alfalfa respond to applications of sulphur or sulphur compounds on many California soils.

Sales of elemental sulphur for soil use in California are shown in table 10.

| Year | Tons | Year | Tons | Year | Tons |
|--|---|------|--|------|--|
| 1924 1925 1926 1927 1928 1929 1930 1931 1932 | $810 \\ 1,919 \\ 493 \\ 400 \\ 642 \\ 1,200 \\ 1,327 \\ 654 \\ 276 \\ $ | 1933 | $572 \\ 1,677 \\ 2,163 \\ 2,496 \\ 2,517 \\ 3,635 \\ 4,562 \\ 5,193 \\ 7,535 $ | 1942 | $\begin{array}{c} 7,720\\ 18,364\\ 36,974\\ 24,056\\ 26,126\\ 23,519\\ 20,304\\ 16,988\end{array}$ |

Table 10. Tons of soil sulphur reported in California.

Most of the tonnage is a straight sulphur containing impurities less than 1 percent, but a small portion is crude sulphur ore containing about 50 percent sulphur. These figures do not include sulphur sold as an economic poison for control of mites, fungi, and other pests. Accurate data are not available on tonnages of economic poisons, but it has been estimated that approximately 10,000 tons of dusting sulphur are used annually in California for pest control. This ultimately finds its way into the soil.

Many other agricultural minerals, such as gypsum, sulphuric acid, and metallic sulphates; commercial fertilizers, such as ammonium sulphate and single superphosphate; and pest control materials, such as limesulphur solution and copper sulphate, are sulphur compounds. Thus more sulphur is applied directly or indirectly to soils in California than any other element. Probably more than 125,000 tons of total sulphur, free and combined, were applied in California in 1948. By way of comparison, during the same year there were applied about 85,000 tons nitrogen, 53,000 tons of phosphorie acid, and 14,000 tons of potash.

Inasmuch as the oxidation of elemental sulphur in soil is chiefly a biological process, investigations have been made to determine the possible value of inoculating soil sulphur with bacteria to speed up the oxidation process. However, it has been reported that such treatment was generally of no particular agricultural value. Elemental sulphur oxidizes in several weeks in most soils and in warm weather.

Sulphuric Acid. Sulphuric acid was tried experimentally about 25 years ago for treatment of alkaline soils but no appreciable amount was used for this purpose until 1947 when 1,651 tons were reported sold in California. This increased tremendously during 1948 to 10,614 tons. In 1949,there were 6,683 tons sold.

Most of this tonnage was straight commercial acid but some was waste acid sludge from petroleum refineries. The sludges contain varying percentages of aromatic compounds and care must be taken to avoid application of excessive amounts of impurities which may injure plants. Some sludges contain a small percentage of organic nitrogen compounds, but the agricultural value of the nitrogen compounds has not been demonstrated.

The acid is applied either by spraying it directly onto the soil or by metering it into the irrigation water. When it is sprayed directly, it is usually applied at the rate of approximately 200 gallons or $1\frac{1}{2}$ tons per acre. When it is applied to the water, enough is added to increase the acidity to pII 2. Care is taken not to apply it in concrete irrigation lines because of the detrimental effect of the acid on the concrete. Large dosages are not applied to growing crops because it may injure them, but they are added to the soil at least 2 months before planting.

The grade of commercial acid usually sold has a density of 66° Baumé and contains H_2SO_4 , 93 percent. One gallon weighs 15.2 pounds and contains 14.2 pounds of sulphuric acid. Therefore, each gallon contains 4.64 pounds of combined sulphur. Prices naturally vary according to grade of material and amount purchased, but the 93 percent material usually sells for about \$19 per ton in carload lots.

Vermiculite. Expanded vermiculite is a mica which has been expanded or popped by heat to form a bulky, porous mineral material. It is used for heat and sound insulation, and for light-weight concretes and plaster. Small amounts have been sold as an agricultural mineral for improving the texture of heavy clay soils in gardens. It provides no plant foods or other chemical elements to the soil. Like pumice, its agricultural value appears to be due solely to its physical nature. 1951]

Expanded vermiculite is particularly useful for rooting cuttings and germinating seed. Its light, porous nature makes it convenient to subirrigate trays or flats in nursery practice and facilitates replanting of rooted cuttings and seedlings.

Zinc Compounds. So many erop trees in California respond to application of zine sprays that some investigators consider zine deficiencies in this state of major importance, although zine deficiencies may be corrected with very small amounts of the element.

As in the case of other micronutrient deficiencies, trees may show symptoms of acute deficiency although the soil in which they are growing contains an abundance of zinc compounds. Apparently some soils have the ability to fix large amounts of zinc in a form in which it is not available to plants. The California Agricultural Experiment Station states that heavy applications of zinc sulphate to the soil cannot generally be depended upon to keep trees healthy, and soil treatments are used only in a few locations where experience has shown them to be effective. Correction of the deficiency is usually made by spraying the trees with sprays containing zinc sulphate or zinc oxide, or by driving pieces of metallic zinc into the trunk or limbs of the affected trees.

Inasmuch as only small amounts of zine are needed, the tonnage of zine sulphate used as an agricultural mineral is not impressive.

| Year | Tons of Zinc Sulphate |
|------|-----------------------|
| 1946 | 111 |
| 1947 | 135 |
| 1948 | 108 |
| 1949 | 123 |

Only 23 tons of zine oxide were reported for the same four-year period. It is common practice to incorporate zine sulphate or zine oxide in certain insecticidal or fungicidal sprays for combination treatment for pest control and correction of nutrient deficiency. Zine compounds so used generally have not been included in tonnage of agricultural minerals. Accurate data are not available on the amounts of zine compounds used in this manner, and it may exceed the agricultural minerals tonnages shown in the table.

Zine deficiency has been widely recognized for 18 years in California on deciduous fruit and nut trees, citrus trees, grape vines, and on ornamental trees and shrubs. Many annual crop plants have thrived on the same soil without any symptoms of deficiency, although such annuals have exhibited symptoms of zine deficiency in other places, notably in Florida. The University has announced the first instance of zine deficiency in an annual crop in California was noted on beans in 1948 and the plants responded satisfactorily to a spray of zine sulphate. It has been noted that zine deficiency symptoms frequently appear in plants growing on sites where a corral or Indian camp had been. The reason for this has not been determined.

PUBLICATIONS

A special publication is issued annually presenting results of analyses of official samples of fertilizing materials drawn each calendar year. It includes statistical data on the sales of the various types of commercial fertilizers and agricultural minerals in California, plant

foot equivalents of the tonnages, lists of registered firms, and notes on analytical procedures. The Bureau of Chemistry also publishes an annual report on the administration of the portions of the Agricultural Code pertaining to agricultural ehemicals. A series of occasional announcements provides information on current matters, including the quarterly tonnage data on sales of commercial fertilizers and agricultural minerals. These publications may be seeured without charge from the Bureau of Chemistry, 1125 Tenth Street, Saeramento 14, California.

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AGRICULTURAL GYPSUM

BY ROBERT Z. ROLLINS *

OUTLINE OF REPORT

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ABSTRACT

Approximately 400,000 tons of gypsum are used annually in California as an agricultural mineral. It is derived from local deposits of erude gypsite and also from hard rock gypsum. Materials are registered by the State Department of Agriculture, Bureau of Chemistry, which administers the law governing the labeling and sale of agricultural chemicals. Materials must be registered with the Bureau before being offered for sale. Every lot or container must show the name and percentage of each constituent of agricultural value claimed to be therein. Materials offered for sale are sampled and analyzed by the state to determine if the composition conforms to that guaranteed on the label. Sampling and analytical methods are described.

INTRODUCTION

Gypsum has been used as an agricultural mineral for many years, and farmers sometimes still call it by its old name "land plaster." Benjamin Franklin encouraged its use by applying it on a hillside pasture in the shape of letters so passers-by could read his message written in ridges of higher and greener grass, "This land has been plastered."

California agriculture used only a few thousand tons of gypsum annually until about ten years ago when the tonnage began to increase rapidly. During each of the past 5 years, approximately 400,000 tons of agricultural gypsum have been used in this state, representing an annual outlay of approximately \$2,000,000 for material and application. Thus gypsum has become the most important agricultural mineral in California, from the standpoint of tonnage and cost. The Bureau of Chemistry has devoted increased attention to the labeling and claims made for it to assure compliance with requirements of law for protection of purchasers.

The State Department of Agriculture. Bureau of Chemistry, administers portions of the Agricultural Code pertaining to the labeling and sale of fertilizing materials and pest control materials. The Bureau is

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primarily a law enforcement agency. It does not provide recommendations with regard to agricultural practices nor conduct investigations and field tests other than those incidental to its regulatory duties. Agricultural research and agricultural advisory services are provided by the University of California Agricultural Experiment Station, with headquarters at Berkeley, California.

COMPOSITION

Gypsum is hydrated calcium sulphate. The chemical formula for this compound is $CaSO_4 \cdot 2H_2O$, from which it may be calculated that the pure material contains combined calcium 23.3 percent and combined sulphur 18.6 percent. The chemical formula also shows that the pure material contains combined water 20.9 percent which is part of the mineral structure and not to be confused with ordinary moisture or "free water" that varies according to whether the particular material is wet or dry. A few deposits of gypsum are more or less dehydrated, having lost a portion of the combined water. Since 100 pounds of anhydrous calcium sulphate, $CaSO_4$, may combine with 26.5 pounds of water to form 126.5 pounds of $CaSO_4 \cdot 2H_2O$, pure $CaSO_4$ is sometimes said to have a gypsum equivalent of 126.5 percent, but such usage of pereentage may be confusing unless the significance of its method of calculation is fully understood.

COMBINED SULPHUR EQUIVALENT

Although agricultural gypsum is used for various reasons by different farmers, its value is commonly attributed to its combined sulphur content. Table 1 affords a convenient comparison of percentages on this basis.

IMPURITIES

The impurities in San Joaquin Valley gypsite deposits are mainly silica and other insoluble materials of no agricultural significance. Most of these materials contain a small amount of calcium carbonate, seldom exceeding 10 percent. A typical analysis is:

| | Percent |
|--------------------------------|---------|
| SO ₃ | 33.70 |
| CaO | |
| SiO ₂ and insoluble | |
| Combined water | 15,53 |
| Free water | 2.88 |
| Iron and aluminium oxides | 1.86 |
| CO ₂ | 1.07 |
| MgO | 0.46 |
| Not determined | 1.62 |

Injurious amounts of boron, sodium chloride, or sodium carbonate have not been found, although it is reported that some deposits of gypsum are near deposits of boron minerals.

Mineral deposits contain traces of many elements, some present in small amounts which can be determined chemically and some in traces which can be detected only spectroscopically. Occasionally a registrant of agricultural gypsum obtains a "complete analysis" of his material and proposes to present all the findings on the label as his guarantee. In general this is not acceptable because it may be misunderstood by the average user and be a source of misrepresentation. Claim for the

| | Combined sulphur | | | Combined sulphur | |
|---|---|---|--|---|--|
| Gypsum percent | Percent | Pounds per ton | Gypsum percent | Percent | Pounds per ton |
| 100 95 90 85 80 75 70 | $18.62 \\ 17.69 \\ 16.76 \\ 15.83 \\ 14.90 \\ 13.96 \\ 13.03$ | $372 \\ 354 \\ 335 \\ 317 \\ 298 \\ 279 \\ 261$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $12.10 \\ 11.17 \\ 10.24 \\ 9.31 \\ 8.38 \\ 7.45$ | $242 \\ 223 \\ 205 \\ 186 \\ 168 \\ 149$ |

Table 1. Combined sulphur equivalent.

presence of SiO_2 , Al_2O_3 , Fe_2O_3 , and for traces of such elements as titanium, tungsten, vanadium, nickel, and chromium, may be understood as positive claims for their agricultural value. Their presence may be used erroneously to suggest a superiority of a crude gypsum over other gysums for which such claims are not made.

TERMINOLOGY

Some confusion is caused by use of the term gypsum to mean both the pure chemical compound, $CaSO_4 \cdot 2H_2O$, and the erude mineral mixtures containing varying amounts of the chemical. Strictly speaking, the gypsum deposits in San Joaquin Valley commonly utilized for agricultural purposes in California are more properly termed gypsite because of their loose earthy nature. They are variable mixtures of gypsum and impurities, and low-grade products may contain only a small percentage of actual gypsum.

The mineral form of anhydrous calcium sulphate, $CaSO_4$, is called anhydrite. Some of this is sold as an agricultural mineral in California, but most of the material sold here is either gypsum containing essentially gypsum 100 percent, or gypsite containing gypsum 50 percent to 70 percent. All three forms appear to be of equivalent agricultural value on the soil when compared on an equivalent basis. For example, either 79 pounds of anhydrite or 143 pounds of gypsite containing 70 percent gypsum, would be equivalent to 100 pounds of pure gypsum.

The term calcium sulphate is loosely used to designate both the hydrated form, $CaSO_4 \cdot 2H_2O$, and the anhydrous form, $CaSO_4$, and the ambiguous term should be avoided unless used in a context where its meaning is clear. Section 1025 (e) of the Agricultural Code requires the analysis of gypsum to be stated on the tag in terms of "the percentage of calcium sulphate therein." This phrase is interpreted to mean the percentage of gypsum, $CaSO_4 \cdot 2H_2O$, inasmuch as this is the actual ingredient in most such agricultural minerals.

Gypsum is defined by law as an agricultural mineral. It is not a *fertilizer* and it should not be referred to as such. In the terminology of the law, which is familiar to farmers in the state, the term *fertilizer*, or more properly *commercial fertilizer*, refers to materials containing 5 percent or more of nitrogen, available phosphoric acid, or water-soluble potash, collectively or singly. Commercial fertilizers and agricultural minerals may serve different purposes and the two should not be confused. Gypsum does not contain any nitrogen, phosphoric acid, or potash.

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A reference to gypsum or any other agricultural mineral as a *fcrtilizer* may be a form of misrepresentation and in violation of law. Similarly the term *plant food* is so commonly used to mean the three primary ingredients in commercial fertilizers, that generally it should not be used with reference to gypsum. The term *fcrtilizing materials* is properly used to refer collectively to commercial fertilizers, agricultural minerals, manures, auxiliary plant chemicals, and soil amendments.

Users have sometimes been misled by the ambiguous statements that gypsum contains sulphur or that it contains lime. To the average user, sulphur means elemental sulphur and *lime* means quicklime (CaO) or slaked lime $(Ca(OH)_2)$ and to some it means calcium earbonate $(CaCO_3)$. Gypsum does contain some chemically combined sulphur, but it does not contain elemental sulphur; neither does pure gypsum contain any of these calcium compounds. The problem is further complicated by the fact that gypsum, elemental sulphur, and three liming materials (quicklime, hydrated lime, and limestone, which is calcium carbonate) have distinctly different agricultural uses, and use of one when another is more appropriate may be ineffective or detrimental. Gypsum is not a liming material. Elemental sulphur tends to make soils acid; liming materials tend to make soils alkaline; gypsum has no immediate effect on acidity or total alkalinity of the soil, but its use may influence the form of the alkalinity. The differentiation between these materials by users may be somewhat confused by the fact that some mixtures of the different chemicals have been sold in California. For example, mixtures of ealcium carbonate and gypsum have been marketed here, and a natural mixture of elemental sulphur and gypsum has been brought into the state for agricultural use.

OCCURRENCE

Gypsum deposits are found in many places in the country, and several mines in California produce high-quality gypsum for preparation of plaster, wallboard, and tile. Some of these mines sell a portion of their output for agricultural purposes, but much of the agricultural gypsum utilized in California comes from the western foothill area of the San Joaquin Valley, where there are numerous deposits of gypsite of marketable grade. Some of these gypsite deposits are large and contain material of uniform quality, analyzing approximately gypsum 70 percent; and some deposits are so small, scattered, variable, or of such poor content that commercial exploitation is not feasible.

These deposits are surface beds of fairly loose gypsite and are generally covered with an overburden of soil. In deposits commercially operated, there is usually about 1 or 2 feet of overburden and the usual bed of gypsite is 5 or 10 feet deep, although wide variations are encountered. The overburden is removed by scrapers of many types or by dragline, and the gypsite is then scraped off and loaded directly into trucks. When a scraper is set to remove a thin layer at a time, the material loaded is sufficiently fine for application, and further grinding is unnecessary. To market a material of reasonable uniformity, an operator must be careful to remove all the worthless overburden before loading, not to scrape beyond or below the bounds of the workable deposit, and to avoid any streaks of low-grade material. Otherwise some trucks may be loaded with worthless soil instead of gypsum. Some agricultural gypsum is prepared from hard rock deposits and some is also derived as a by-product from manufacturing processes. It is of interest that approximately half of normal superphosphate is anhydrite and many tons of this are used as a commercial fertilizer in California.

AGRICULTURAL USE

Most of the agricultural gypsum sold in California is used in San Joaquin Valley within trucking distance of local deposits, although a portion of the tonnage is used in other parts of the state. It is applied to improve soil texture, increase permeability to water, alleviate severe elod and crust formation, render the soil easier to work, and to aid in the reclamation of alkali soils. Gypsum reacts with sodium carbonate, commonly called black alkali, to form sodium sulphate, commonly called white alkali, and calcium carbonate, which is the same as limestone. Sodium sulphate is much less injurious to plant life than sodium carbonate, so the conversion is of distinct advantage. Soils alkaline with sodium carbonate are sticky when wet, and set to a hard cake when dry. Addition of gypsum aids in flocculating the mass and tends to make the soil loose and friable.

Gypsum is applied to soils where many of the diversified crops are grown as in the San Joaquin Valley, and particularly on those for potatoes in Kern County where most growers use gypsum primarily to improve penetration by water during irrigation. Gypsum is also used on sulphur-deficient soils to supply this element to alfalfa and leguminous cover crops. The use of gypsum in California is correlated with soil type rather than with any specific crops, but the other crops most commonly grown in the area of greatest use include citrus and deciduous orchards, vineyards, cotton, and vegetables. No accurate data are available with regard to the tonnage of gypsum used on specific crops or in specific counties.

Gypsum is not suitable for reducing acidity of soils. However, most agricultural soils in California are commonly somewhat alkaline, and acid soils are a problem in only a few places in the state. Gypsum may be largely wasted if applied to acid soils or to light loam or sandy soils, unless an actual deficiency of soil-sulphur or soil-calcium is involved.

APPLICATION

The rate of application of gypsum varies greatly depending upon the erop involved, the degree of correction required by the soil, and the purpose for which it is used. In general, applications range from less than 1 ton to as high as 20 tons per acre. Some soils are given but a single application and some are given regular annual applications for several consecutive years. It is possible that a soil might be more or less permanently corrected by a program of annual applications over a sufficient period, but this seems not to have been demonstrated.

Gypsum is usually spread on the soil and turned under by shallow cultivation. It is sometimes applied to soils by means of end-gate spreaders attached to the same trucks that are used to haul it from the mines to the fields, and several special types of equipment have been developed in the San Joaquin Valley to minimize labor in spreading this agricultural mineral. Some application of gypsum has been made by dissolving it in irrigation water. However, only about a quarter of an ounce of gypsum can be dissolved in a gallon of water under most favorable circumstances, which is equivalent to about $2\frac{1}{2}$ tons in one acre-foot of water. This low solubility and the difficulties involved in adequately mixing the gypsum with the incoming water present a problem. Mechanical arrangements have been developed for metering gypsum into irrigation water at the rate of several hundred pounds per acre. This method is particularly useful when gypsum is being added to correct an unfavorable sodiumcalcium ratio in the irrigation water.

If gypsite containing gypsum 70 percent were used in such a manner, the sludge comprised of the 30 percent of the more insoluble impurities might elog the irrigation system. This method of application would seem satisfactorily possible only when high grade gypsum is used, and only when low rates of application are desired.

Much of the gypsum is applied during the winter months when trucking facilities are readily available, but some is applied throughout the year as may be seen from the quarterly tonnage statistics published by this Bureau.

COSTS

The costs of transportation from the mine and of spreading on the farm are usually greater than the price of gypsum at the source, and these eharges must be added to the original cost of any material in making an estimate of what the grower pays to get gypsum onto his land. If a grower receives low-grade gypsum, he not only loses a portion of what he paid for the material, but in addition pays excessive transportation costs in hauling worthless impurities as well as the added cost of spreading the impurities. A 10-ton load of an agricultural mineral eontaining only gypsum 40 percent involves hauling and spreading 6 tons of worthless material. Since hauling charges for gypsite from San Joaquin Valley deposits are usually more than the cost of the material at the source, low-grade gypsum can be more costly than high-grade gypsum. Gypsum may be legally sold with a guarantee as low as 20 percent or 30 percent but cost of hauling and spreading the worthless 80 percent or 70 percent generally makes its use uneconomical.

Crude gypsite containing gypsum 50 percent to 70 percent commonly sells for about \$1.75 per ton at the mine. and about \$6 per ton delivered to the farm. High grade agricultural gypsum (93 percent) in 100-pound bags commonly sells for about \$14 per ton delivered. Prices naturally vary according to analysis, location, and amount purchased.

SOIL CONSERVATION PROGRAM

In accordance with the soil conservation program, the Federal Production and Marketing Administration makes certain payments to farmers who apply soil sulphur or its equivalent as combined sulphur in the form of gypsum to an existing stand of, or in connection with a full new seeding of, perennial or biennial legumes, perennial grasses, green manure crops in orchards, permanent pastures seeded alone or with a nurse crop, and winter legumes; or where the County Committee determines such application is necessary to correct alkali soil conditions. 1951]

Information is not available to show what percentage of the gypsum used in California was eligible for payments under the P. M. A. program in 1949, but partial data indicate that about half the gypsum used in San Joaquin Valley in 1947 was used in an eligible manner. Payment is made on a basis of the amount of sulphur equivalent, and it is reported that in 1947 payment was made on 210,847 tons of gypsum (18 percent combined sulphur) applied to 294,690 acres on 4,452 farms. In 1946 payment was made on 23,751 tons of "available sulphur" applied on 5,250 farms, on 219,630 acres.

STATISTICS OF SALES

The law requires each registrant of agricultural minerals to submit a quarterly statement of sales and pay a tonnage license tax of 10ϕ per ton. These reports are regularly audited. The private business of individual firms is safeguarded by publishing figures only for those types of agricultural minerals reported by three or more firms, but gypsum has always been reported by a large number of firms. The tonnage of agricultural gypsum sold in California during the last 25 years is shown in table 2.

In the same 25-year interval, the total tonnage of all agricultural minerals sold in California increased from 44,241 to 422,484 and the tonnage of commercial fertilizers increased from 66,274 to 511,460. In 1924, gypsum represented approximately 10 percent of the total tonnage of agricultural minerals. In 1949, it represented approximately 80 percent.

The tonnage of gypsum handled in 1948 may be better visualized by considering that it was equivalent to about 40,000 truckloads of 10 tons each, or more than 100 truckloads per day every day in the year. Assuming a probably average haul of 50 miles, this represents a total haul of about 2,000,000 miles.

| Year | Tons sold | Year | Tons sold |
|------|-----------|------|-----------|
| 1924 | 4,085 | 1937 | 24,218 |
| 1925 | 6,504 | 1938 | 17,580 |
| 1926 | 11,049 | 1939 | 42,878 |
| 1927 | 10,185 | 1940 | 77,195 |
| 1928 | 14,120 | 1941 | 122,304 |
| 1929 | 15,269 | 1942 | 185,856 |
| 1930 | 11,449 | 1943 | 300,980 |
| 1931 | 5,583 | 1944 | 395,174 |
| 1932 | 4,410 | 1945 | 367,108 |
| 1933 | 3,618 | 1946 | 414,286 |
| 1934 | 7,914 | 1947 | 490,268 |
| 1935 | 16,787 | 1948 | 394,979 |
| 1936 | 17,328 | 1949 | 338,340 |

| Table 2. | Tonnage of | ⁱ agrieulturai | gypsum | sold in | California. |
|----------|------------|---------------------------|--------|---------|-------------|
|----------|------------|---------------------------|--------|---------|-------------|

The tonnages in table 2 represent erude gypsum as sold. The available data do not permit an accurate calculation of the actual gypsum equivalent for each year, but in recent years approximately threequarters of the tonnage has been San Joaquin gypsite containing gypsum about 70 percent and one-quarter has been higher grade material containing 90 percent or more.

REQUIREMENTS OF LAW

Gypsum is elassified by the Fertilizing Materials Article of the Agricultural Code as an "Agricultural Mineral." It must be sold in accordance with the provisions of this law, which requires among other things that:

(1) Gypsum must be from the supply of a person or firm who has obtained from the Bureau of Chemistry a certificate of registration for agricultural minerals, and who has registered each composition to be sold.

(2) Gypsum can be sold only by the holder of a fertilizer salesman's license. There are several exceptions: a registrant may sell his own registered products without a fertilizer salesman's license and such a license is not required for a dealer to sell gypsum in a registrant's package from a fixed place of business.

(3) Each lot or bag of gypsum must bear a tag stating the percentage of gypsum (CaSO₄·2H₂O), and the name and address of the registered producer. If the material is sold in a loose lot, a tag bearing the required information should be firmly attached to a stake driven into the pile so as to be plainly visible while in transit and upon delivery to the user.

(4) A tonnage license tax of 10ϕ for every ton sold must be paid quarterly by the registered producer.

It is a misdemeanor to make any misrepresentation in connection with the sale of any fertilizing material. For example, it is not acceptable to elaim that gypsum "contains sulphur" or that it "contains plant foods" or that it is a "fertilizer" if such elaims are made in a manner that may lead the purchaser to believe the material contains elemental sulphur, nitrogen, phosphoric acid, or potash.

ADMINISTRATION OF LAW

The Bureau of Chemistry administers the Fertilizing Materials Article of the Agricultural Code as well as certain portions of the Code pertaining to other agricultural chemicals. The main office and laboratory of the Bureau are in Sacramento. Branch offices are in Los Angeles, San Francisco, and Visalia. Inspectors travel throughout the state and regularly draw official samples of gypsum, as well as other agricultural chemicals offered for sale in California. The official samples are analyzed in the laboratory and the results of analyses are sent to the user of the particular lot sampled, to any dealer who may be concerned with the particular lot, and to the registered producer. There is no charge for this service. If analysis shows that there is a deficiency of economic significance in the lot sampled, the registrant is requested to produce evidence that proper adjustment has been made to the purchaser.

In order to permit reasonable leeway for unavoidable variations in marketing, the law provides that a lot of gypsum is not to be considered deficient unless the percentage is low by more than 5 percent of the guarantee. For example, if a lot is guaranteed to contain gypsum 70 percent and contains less than 66.5 percent, it is deficient and to sell it or to offer it for sale is a violation of law.

All claims made with regard to gypsum and other fertilizing materials are subject to jurisdiction of the law. The Bureau examines

advertisements in periodicals, advertising distributed in the form of cards, leaflets, bulletins, or letters, and also considers radio advertising, salesmen's verbal claims, and all other claims made directly or indirectly in connection with the sale of these agricultural chemicals. Prompt action is taken against misrepresentation in any form in order that farmers in California may purchase agricultural chemicals with confidence and satisfaction.

Criminal complaints are filed when necessary to secure compliance with law. Repeated violations by firms dealing in gypsum have resulted in cancellation of certificates of registration, without which any sale is a misdemeanor. Constant vigilance and thorough enforcement of law not only discourages violations and secures some compensation of purchasers for economic cheats in the materials they buy but, by its presence alone, a well-administered law serves to minimize attempts of fraud and misrepresentation.

SAMPLING

Much of the gypsum used in California is hauled loose in truckload lots directly from the mine to the field on which it is to be used, so it remains in the channels of trade and subject to inspection and sampling for a shorter time than other agricultural chemicals. Inspectors must arrange their sampling activities according to availability of the material for inspection. Samples are usually drawn from truckloads en route and occasionally from lots delivered and left intact at farms. Some gypsum is sold in bags, and this material is subject to inspection and sampling wherever found in hands of dealers or purchasers.

Section 1037 of the Agricultural Code provides that if the fertilizing material is packaged in containers of less than 10 pounds, one package of the material may be taken as a sample to represent the lot of which it is a part, but gypsum is seldom sold in small packages.

When gypsum is packaged in containers of 10 pounds or more, each official sample consists of at least 1 pound of material taken in the following manner: A sampler is used to remove a core diagonally from end to end of the bag. Cores are taken from all bags if 20 or fewer are present. If 21 to 200 bags are present, 20 cores are taken from as many bags. If more than 200 bags are present, cores are taken from 20 bags plus 1 bag for each additional ton in excess of 10 tons. The portions are thoroughly mixed on a clean rubber sheet, oil cloth, or paper, and reduced by quartering to the quantity of sample required. Opposite quarters are placed in one sample container and the remainder in another for a duplicate sample.

When gypsum is sold in a loose lot by truckload or earload, the load constitutes one package. An official sample is taken in the following manner: The outer surface is scraped aside before inserting sampler, because the load may have been wet with a hose to reduce dust or the wind may have blown the fine material from the surface, and at least 20 approximately equal cores are taken from fairly evenly distributed parts of the quantity. If more than 10 tons are contained in a lot, two cores are taken for each additional ton. Portions are taken with a trowel when the material contains large lumps or when for other reason it is not possible to use a sampler. Lumps are broken if necessary and the material is mixed, quartered, and placed in sample containers. An official sample of a fertilizing material is sealed before removal from premises where it was drawn. The seal bears the date; name of product as given on the label, if any; signature of person acknowledging the sample; inspector's initials and sample number. The duplicate portion is sealed and left with the party whose stock was sampled or left on the premises where it was drawn.

A total of 180 official samples of gypsum were drawn and analyzed during 1948; these represented a total of 10,256 tons. Since 394,979 tons of gypsum were sold in California during 1948, it can be seen that 2.6 percent of the total tonnage was specifically examined by this Bureau. For every sample of gypsum drawn and analyzed during the year, approximately 2,194 tons were sold. By way of comparison, one sample of commercial fertilizer was drawn for every 262 tons sold. In general, commercial fertilizers are more expensive and more important to farmers than agricultural minerals, and the purpose of the law is served most effectively and economically by sampling the more important materials more intensively.

ANALYSES FOR USERS

The law provides that a person who is actually using or intends to use an agricultural mineral for fertilizing purposes may submit a sample for analysis to determine conformity or nonconformity of the material to the guarantee under which it is sold or is to be sold. The user submits information with regard to the lot of material, a copy of the tag, and the service fee which is \$4 for analysis of gypsum. Users rarely submit samples for analysis because a report issued on such a sample does not have the legal status of a report issued on an official sample drawn directly by the Bureau, and no charge is made for official samples.

METHOD OF ANALYSIS

The routine method of analysis used for examination of any sample depends somewhat upon what is definitely known about the material. For example, if it is known that the material contains no sulphur compounds other than gypsum, it would probably suffice to determine only the combined sulphate-sulphur and to calculate the percentage of gypsum from that. If the mixture may contain other sulphates, elemental sulphur, or sulphite-sulphur, the analytical method must be adapted accordingly. Occasionally there may be need to differentiate between various calcium compounds in a material purported to be gypsum. Total combined earbon dioxide may be determined to estimate carbonates. Elemental sulphur is found in a few materials and it is possible that magnesium compounds may be present in others. Special materials naturally require special methods; however, the following method is generally satisfactory for routine samples of agricultural gypsum.

It has been found that some free water is lost from moist samples during the process of grinding the material for analysis, which tends to give slightly higher results for the percentage of gypsum determined. This error has been largely avoided by determining the free water first so the percentages can be calculated on the basis of the material as received.

Determination of Free Water. Rapidly weigh in a flat dish a 10-gram portion taken with a small tryer from the sample jar. Dry the material for 4 hours at 45°C., and report the proportional loss in weight

as 'Free water.'' This does not include the combined water which is part of $CaSO_4 \cdot 2H_2O$.

Preparation of Sample. Pass the entire remaining material through a 10-mesh sieve. Thoroughly mix and quarter the material and grind a portion to pass through a 60-mesh sieve. Place about 10 grams of this ground material in a flat dish and dry for 4 hours at 45°C. Use portions of this dried material for determination of combined sulphur and combined calcium.

Determination of Combined Sulphur. Weigh a 0.5000-gram portion of the dried material and transfer it to a beaker. Wet it with water and add excess dilute hydrochloric acid carefully to avoid loss by possible effervescenee of earbonates. Cover the beaker with a watch glass supported on a glass triangle and evaporate carefully to dryness on a hot plate at low heat to prevent spattering. Bake the residue for several minutes to decompose silicic acid. Dissolve it in hot water with a few drops of hydrochloric acid. Filter and wash the insoluble material thoroughly. Dilute the filtrate to approximately 500 milliliters. Heat to boiling and while boiling, slowly add 10 milliliters of 10 percent barium chloride solution with constant stirring. Cover the beaker and set it on a boiling water bath overnight or for several hours. Filter through a fine paper. Transfer the precipitate to the filter and wash it free of chlorides with hot water. Ignite the filter and precipitate at dull redness and weigh the residue as barium sulphate. The gravimetrie factor 0.1374 converts barium sulphate to combined sulphur. Inasmuch as the sample weighed 0.5000 gram, the percentage of combined sulphur calculated on the basis of the original material is :

 (grams BaSO_4) (27.46) (100 - percent free water)

Similarly the percentage of gypsum, $CaSO_4 \cdot 2H_2O$, equivalent to this percentage of combined sulphur is:

 (grams BaSO_4) (147.5) (100 - percent free water)

This indicated percentage of gypsum is tentative as discussed later.

Determination of Combined Calcium. Weigh a 0.4000-gram sample of the dried material and transfer it to a 500 milliliter Erlenmeyer flask. Wet it with water and add sufficient dilute hydrochloric acid containing a little nitric acid to dissolve the gypsum, and boil. Dilute to 200 milliliters and heat. Add 25 milliliters saturated ammonium oxalate solution and slowly add ammonium hydroxide to the hot solution until it is neutral to methyl red. Allow the solution to cool and to stand for 4 hours. Filter through a medium-fine paper and wash the flask and the filter thoroughly with cool water. Rinse the precipitate back into the flask with hot water. Acidify with dilute sulphuric acid and titrate the hot solution with standard potassium permanganate solution until pink. Add the filter, stir to a pulp, and continue titration to a faint pink color. Inasmuch as 1 milliliter of tenth-normal potassium permanganate is equivalent to 0.002004 gram combined calcium, and the sample weighed 0.4000 gram, the percentage of combined calcium ealculated on the basis of the original material is :

 $(ml. N/10 KMnO_4)$ (0.5010) (100 - percent free water)

Similarly the percentage of gypsum, $CaSO_4 \cdot 2H_2O$, equivalent to this percentage of combined calcium is :

 $(ml. N/10 \text{ KMnO}_4)$ (2.152) (100 - percent free water)

This indicated percentage of gypsum is tentative as discussed later.

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Calculations. The percentage of gypsum indicated by the combined calcium in most official samples is slightly higher than that indicated by the combined sulphur because most of the agricultural materials contain small amounts of calcium earbonate. The lower of the two percentages is reported as the percentage of gypsum, $CaSO_4 \cdot 2H_2O_1$, in the material. No attempt has been made to distinguish between gypsum and anhydrite.

PUBLICATIONS

The results of analyses of official samples of commercial fertilizers and agricultural minerals drawn during each calendar year are published annually by the Bureau. These analyses serve not only as a guide in administration of the law, but are an important source of information to users. Farmers can readily compare analyses of different types of materials, and compare the records of different registrants in meeting the guarantees made for their materials. Interested persons familiarize themselves with the law governing sales of gypsum to assure value received for the money they spend when buying their supplies.

Copies of the law, annual reports of this Bnreau, lists of registered firms and of registered products, special publications providing analyses of official samples, announcements with regard to special items of interest, and other informative publications of agricultural chemicals are available upon request from the Bureau of Chemistry, 1125 Tenth Street, Sacramento 14, California.

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GYPSUM RESOURCES OF CALIFORNIA

BY WILLIAM E. VER PLANCK

Consumption of agricultural gypsum in California during 1948 amounted to 394,979 tons or about a third of the total consumed for all purposes. More than three-fourths of the agricultural gypsum consumed in the state is low grade material containing from 40 to 70 percent gypsum and mined only for agricultural purposes from deposits within 200 miles of the farms. The remainder is material containing 90 percent or more of gypsum, and at present almost all of it is sold by producers in Imperial County, eastern Riverside County, and Nevada who are primarily engaged in the plaster industry.

Gypsum (CaSO₄·2H₂O) is among the more soluble rock forming minerals, and therefore outcrops of gypsum are seldom found except in arid regions. Most commercial gypsum is a massive, often impure, opaque white to gray material known as rock gypsum. Gypsite, an important source of agricultural gypsum, consists of an earthy mixture of very small gypsum erystals and sand or elay that forms efflorescent deposits. Other less common varieties of gypsum are the platy transparent type known as selenite, the fibrous type known as satin spar, and the massive white, sometimes translucent, type known as alabaster. Gypsum is commonly associated with anhydrite (CaSO₄), a mineral believed to be comparable to gypsum in its value as an agricultural mineral, when compared on an equivalent basis. Little anhydrite, however, has been sold in California.

The natural ealeium sulfate minerals have most commonly formed through the evaporation of sea or saline lake waters, but they also occur as part of the gangue in hydrothermal veins, in near-surface veins formed by deposition from ground water, and as replacements of limestone. In saline deposits at least part of the ealeium sulfate is believed to have originally precipitated as anhydrite and to have been altered to gypsum by the action of ground water.

Gypsite forms only in regions of little rain and high evaporation. Capillary action draws calcium sulfate-bearing ground water toward the surface where very small crystals of gypsum form. In addition to sand and dirt, gypsite often is contaminated with calcium carbonate. Much less frequently it contains borates or chlorides.

Deposits of gypsite are particularly numerous along the west side of the San Joaquin Valley from Ortigalita Creek in Merced County to McKittrick. Gypsite also occurs along Cottonwood Creek east of Bakersfield; near Carrizo Plain and Shandon, San Luis Obispo County; in the playa at Saltdale, Kern County; near Palmdale. Los Angeles County; and near Corona. Riverside County. Deposits in the San Joaquin Valley now being worked include the H. M. Holloway Inc. Lost Hills mine at Lost Hills and Avenal Gap mine in Kettleman Plain, deposits of the McKittrick Agricultural Gypsum Company and Western Gypsum Company near McKittrick, the Pacific Gypsum Company's deposit at Kern Lake, C. L. Fannin's deposit in Packwood Canyon, R. P. Jones' Valley View mine in the Panoche Hills, the Griffin deposit near Tumey Gulch, and the Agricultural Minerals and Fertilizer Company's deposit near Little Panoche Creek. Outside the San Joaquin Valley are the Vanderford deposit at Shandon, San Luis Obispo County, and the Daly deposit near Saltdale, Kern County.

Three types of gypsite deposits are recognizable. Most numerous are those that have formed on the outerops of beds containing disseminated gypsum in the form of selenite crystals and plates along fractures or as part of the cement of sandstones. Examples include some of the McKittrick deposits and the deposits in the Panoche Hills, Carrizo Plain, and at Palmdale.

Relatively large gypsite bodies have formed along the margins of periodic lakes. Gypsite deposits on the south margin of Kern Lake, at the playa near Saltdale, and probably also in Kettleman Plain belong to this class. The Lost Hills deposits have some of the features of this type.

A third type is represented by two deposits at McKittrick which occur in the beds of dry washes.

The gypsite deposits that have formed on the outcrops of gypsiferous beds closely parallel the present surface except that the overburden is likely to be thinner high on hillsides than it is toward the base. At one place at McKittrick gypsite crops out near the summit of a hill, but at the base it lies beneath 5 feet of overburden. The contact between the gypsite and the underlying rock is generally gradational. Most of the gypsite in the McKittrick area lies on fine sandy to gravelly soil, although in one small area it rests directly on steeply dipping shale. At the Valley View mine in the Panoche Hills the gypsite becomes sandy toward the bottom. The sandy gypsite lies on soft sandstone cut by satin spar veinlets of gypsum or on gravel containing fragments of selenite.

Individual gypsite bodies may cover several acres, but some bodies are mere patches less than 100 yards in diameter. The average maximum thickness is 3 or 4 feet, but rarely the thickness may reach as much as 8 feet in a limited area.

The gypsite itself is tan to cream in color and is usually soft. It is composed of unconsolidated crystals of gypsum 0.002 inch or less in length, mixed with quartz grains. Calcium carbonate is often present. especially in low grade gypsite.

Gypsite bodies that occur on the margins of periodic lakes are flat irregular lenses which lie with a sharp contact on lake beds. Sometimes the gypsite crops out, but usually it is covered with up to 3 feet of sandy soil. Specimens of gypsite from these deposits resemble that which forms on outcrops except that the gypsum crystals of the lake margin type are a little larger.

In the Avenal Gap deposit in Kettleman Plain the upper part of the gypsite body is a hard gray impure gypsite which changes within a 6-inch transition zone to the soft yellow-white gypsite that forms most of the deposit. At Kern Lake the purest gypsite is found near the top. Toward the bottom contact the gypsite becomes harder and less pure.

Both the Kern Lake deposits and the Avenal Gap deposit contain solution cavities. Those at Kern Lake are sinks as large as 3 feet in diameter. Some of the tunnel-like holes in the Avenal Gap deposit are filled with unconsolidated sand. This deposit also contains lenses of sand.

The Lost Hills deposits of H. M. Holloway, Inc., who is the largest producer of gypsite in the state, occur along the west side of the Lost Hills and are in general elongate in a direction at right angles to the trend of the hills. The gypsite, which may be as much as 20 feet thick, is covered by up to 20 feet of slightly consolidated silty sand. Clean, soft gypsite at the centers of the bodies grades outward into gray silt containing streaks and spots of finely crystalline gypsum. Lenses of gravel are found within the gypsite, and in places gravel lies beneath the gypsite and the clay that occurs beneath the gypsite.

Two of the deposits at McKittrick are long, narrow, crooked bodies that closely follow the beds of dry washes. Gypsite occurs on the surrounding hills and the gypsite in the channels may have been washed from the hills. The channel gypsite may also have originated from gypsiferous ground water that accumulated in the channels.

The channel deposits are covered by a thickness of as much as 5 feet of slightly consolidated sand containing rock fragments. The gypsite, which is soft and light colored, grades at the bottom into gypsiferous sand and clay. Where exposed, the underlying material is creek gravel containing pieces of selenite up to an inch long.

Rock gypsum deposits of Tertiary age include the United States Gypsum Company's mine in the Fish Creek Mountains, Imperial County, the largest gypsum mine in the state. This deposit, which is at the north end of the Fish Creek Mountains, is part of a formerly much more extensive deposit that has been dissected by erosion. In the mine area the gypsum beds have been preserved in a shallow synclinal basin 3 miles long and half a mile wide. The beds, except for violent local contortions in the gypsum, dip uniformly at angles of from 25° to 35° toward the synclinal axis.

The gypsum is included in Miocene beds that have been differentiated by Dibblee.¹ They lie on a pre-Cretaceous basement of metamorphic rocks intruded by coarse gneissic granite. The gypsum is underlain by the Split Mountain formation which in its lower part consists of coarse, arkosic, red-weathering sandstone with conglomerate beds composed of cobbles of all the older rocks. The upper part is a gray boulder conglomerate with subordinate layers of gray arkosic sand. In most places such sand immediately underlies the gypsum. Overlying the gypsum is the Imperial formation containing elay beds alternating with limonite-cemented quartz sand. These beds have been largely removed by erosion. Eastward the underlying Split Mountain formation pinches out and is overlapped by the gypsum.

Other large but inaccessible remnants of the original deposit are known to exist to the south, and there may be extensions westward into San Diego County.

Another Tertiary deposit is that of the Monolith Portland Cement Company in Quatal Canyon near Cuyama Wash, Ventura County. This deposit eonsists of a single bed of massive brown gypsum 10 to 30 feet thick that may be traced for at least 7 miles. The gypsum is contained in a brown clay, and the elay in turn is contained in a great thickness of coarse, slightly indurated sandstone. The entire output of gypsum from this operation is used as a retarder in the manufacture of portland cement. The Blue Diamond Company owns patented claims adjoining the Monolith Portland Cement Company's property on the northwest.

A second gypsiferous horizon in the Cuyama Wash region lies about 5 miles southwest of the Quatal Canyon deposit. It consists of thin beds and impure beds of gypsum from which gypsite deposits have been derived. Masses of alabaster up to a maximum of 10 feet in largest dimension also occur in it. Exploratory work has been done in numerous places,

¹ Dibblee, T. W., Jr., Geology of Split Mountain area: unpublished map, 1944.

but only a small tonnage of gypsum has been shipped. The terrestrial clays that contain both groups of gypsum deposits grade into marine sediments northwestward along the strike; to the southeast the clays become coarse.²

In the northern foothills of the Avawatz Mountains, San Bernardino County, gypsum, together with salt and celestite, occurs in lake beds involved in the complicated structures along the Garlock and related faults. Gypsum and interbedded gypsiferous clay occur in two roughly parallel zones 9 miles long and in places up to 400 feet thick. Celestite is interbedded with the gypsum in the western part of the deposit, but the salt is in fault contact with the gypsum bodies. The lake beds consist mostly of bright-colored yellow, gray, and red clays. Although there has been much development work, there has been no production.

A deposit at China Ranch, Invo County, was worked during 1916 and 1917. Here a great thickness of brown clay shale contains gypsum beds totaling 20 feet in thickness. Individual beds from 6 inches to 3 feet thick are separated by as much as 3 inches of shale. The gypsum is white and of medium grain size. The beds dip at angles up to 25° .

Similar but smaller Tertiary deposits are found at Owl Holes, Copper Canvon, and Furnace Creek in the Death Valley area. Other Tertiary deposits, some of which have been worked, are near Point Sal, Santa Barbara County; Fillmore, Ventura County; in Mint Canyon, Los Angeles County; and on the Mule Shoe Ranch, San Benito County.

Pre-Tertiary deposits of gypsum occur in the Little Maria Mountains, Riverside County, where the Midland operations of the United States Gypsum Company and the American Gypsum Company's mine are located. The gypsum beds form part of a series of slightly metamorphosed sediments that cross the range from east to west. The sediments are bordered on the north by granitic rocks and on the south by gneissic granite. The rocks of the gypsum belt are beds of quartzite, crystalline limestone, and quartz-albite-mica schist, which dip to the northwest at angles of 50° to 80°. Gypsum occurs in the limestone as persistent beds up to 50 feet thick and in the schist as lenticular bodies which have a more limited extent along the strike. The gypsum is a coarse-grained snow-white aggregate of transparent grains. Often it contains thin layers and lenses of schist, and schist is present also in gypsum interbedded with limestone. Anhydrite is present at depth and is the mineral from which the gypsum has formed. In the United States Gypsum Company's underground workings there is evidence that the extent of alteration of anhydrite to gypsum depends on the presence of fractures and other openings that permit the access of water.

Similar but undeveloped deposits have been found in the Maria Mountains, the Palen Mountains, and the Riverside Mountains, Riverside County.

Prior to 1924 the largest single source of gypsum in California was the crystal body of Bristol Lake, San Bernardino County.³ Gypsum was found in the northern and eastern parts of the playa and within half a mile of the shore. Gypsum lies beneath a foot or two of salty sand and extends to an unknown depth below the water level which is 6 to 8 feet

² T. W. Dibblee, Jr., personal communication. ⁸ Hess, F. L., California, in Stone, R. W., and others, Gypsum deposits of the United States: U. S. Geol. Survey Bull. 697, pp. 81-83, 1920

below the surface. The character of the gypsum varies from clean white granular gypsum to salty dirt containing gypsum crystals. Gypsum crystals are sometimes an inch or more in maximum dimension. This gypsum had to be washed free of salt and dirt before use. A similar deposit is said to exist in the neighboring Danby Lake.

Because gypsum is a low-cost commodity inexpensive methods of mining and preparation are practiced. To date the only beneficiation found practicable has been screening and hand sorting.

For gypsite, current practice is to use carryall scrapers both for mining and for removing the thin overburden. Little development is necessary other than stripping and the construction of access roads and truck loading ehutes. Nearly all of the gypsite is used without any treatment whatever but one operator has installed a $\frac{3}{4}$ -inch screen to remove stones.

Rock gypsum must be drilled and blasted. The Fish Creek Mountain deposit has been developed by means of an open cut which in 1942 was 3,000 feet long and 100 feet high.⁴ At that time the practice was to break a large tonnage by blasting a series of churn drill holes. Smaller mines use wagon drills or jackhammers; and smaller, less regular benches are maintained. Steeply dipping deposits are mined by the open stope method or more rarely by shrinkage stoping.

Rock gypsum for agricultural use is finely ground, often 90 percent through 100 mesh. Jaw crushers are used for primary crushing. Grinding is done with hammer mills. Grinding may be done in closed circuit with an air separator. Usually agricultural gypsum is packed in paper bags but some is shipped in bulk.

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⁴ Sampson, R J., and Tucker, W. B., Mineral resources of Imperial County: California Div. Mines Rept. 38, p. 135, 1942.

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LIMESTONE AND MARL RESOURCES OF CALIFORNIA

BY OLIVER E. BOWEN, JR.

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INTRODUCTION

California is well supplied with natural lime-bearing materials suitable for agricultural use. Not only are there large deposits of crystalline limestone, shell limestone, shell marl, and unconsolidated seashells, but one or another of these types of deposits is present in nearly all parts of the state. As agricultural limes sell at a low price, this broad distribution of deposits is fortunate; high prevailing freight rates will not reconcile long distance hauling with a low-priced delivered product.

Although most California soils are not deficient in line for growing most plants and as acid soils are of limited distribution here, line is not so universally used in quantity as it is in many humid midwestern states. However, conditioning of California soils with line is becoming more widespread with prolonged tilling in intensively farmed areas and with increased intensive gardening in "heavy" or clay-rich soils.

Slightly more than half of the present agricultural lime consumption comes from by-products, that is, lime-bearing residues from various physico-chemical processes such as sugar refining. Between natural and by-product limes, California is adequately supplied to allow for almost unlimited expansion in agricultural lime usage. In 1949, 10,495 tons of limestone and 11,741 tons of manufactured lime were sold in California.

OCCURRENCES AND ORIGIN OF NATURAL LIME MATERIALS

Crystalline limestone, shell limestone, loose shells, shell marl, marl, caliche, travertine, calcareous tufa, dolomite, and dolomitic limestone have all been used in California as sources of agricultural lime. Of these many materials, crystalline limestone, shell limestone, shell marl, and loose shells supply more than 90 percent of all natural materials currently utilized.

Crystalline limestone is detrital or biochemically deposited calcium carbonate (or both), which has been changed by earth processes involving heat and pressure into a mass of interlocking crystals of carbonate minerals among which calcite (CaCO₃) greatly predominates. Grain size in crystalline limestones may vary in average diameter from less than 1 millimeter to several inches. Crystalline limestone is the most abundantly present and widely distributed source of lime in California, being found in Paleozoic and Mesozoic crystalline complexes in almost all major mountain chains of the state. The principal crystalline limestone districts are the Klamath Mountains from Yreka to Redding, particularly in the McCloud, Hosselkus, and Kennett formations; the western Sierra Nevada from Plumas to Kern County, particularly in the Calaveras limestone of Tuolumne, El Dorado, and Calaveras Counties; the south central Coast Ranges of San Benito, Monterey, and Santa Cruz Counties, particularly in the Gabilan limestone; the desert ranges of Inyo, San Bernardino, east Riverside, and Imperial Counties which include countless localities; the Transverse Ranges of southern California, particularly the Wrightwood district of the San Gabriel Range and the Cushenbury district of the San Bernardino Range; the San Jacinto-Santa Rosa Mountain area of east Riverside County, particularly the area northeast of Lake Hemet; and, the Colton-Riverside area of the Jurnpa Mountains, Riverside County.

Fine grained unmetamorphosed or weakly metamorphosed limestones are locally present in various Tertiary formations of Ventura, San Luis Obispo, and Santa Barbara Counties, and in small lenses in the Franciscan formation throughout the Coast Ranges. With the exception of the Permanente deposits in Santa Clara County, concentrations of this type of rock in California are comparatively small.

Shell-limestone or ecquina is merély an accumulation of seashells cemented together by calcium carbonate. Most California shell limestones are of Tertiary age but a few are Cretaceous. In some instances shell limestone incorrectly has been called marl in California, and some of the California lime production which has been sold as marl was shell limestone. The latter is widely distributed in California, but in a majority of cases the accumulations are in thin beds that are not economically feasible to exploit. In some cases, however, shell limestone bodies have proven large enough to allow sustained production on a moderate scale. Several localities in Ventura, Santa Barbara, and San Luis Obispo County currently produce shell limestone for agricultural purposes. The "Tapo" beds of Tapo Alto Mountain, Ventura County, are a well known source of agricultural limestone. Lime Mountain and Lopez Canyon in San Luis Obispo County are two other localities where shell limestone recently has been quarried.

In various estuaries along the California coast shells of brackish water molluses have accumulated in notable quantities. Dredges in San Diego Bay, Newport Bay, and San Francisco Bay commonly uncover deposits of this sort. Along the southeastern shores of San Francisco Bay harvesting of seashells for their lime content has become a million-dollara-year business. Agricultural lime and industrial lime are produced as by-products of the major cement industry at Redwood City and intermittently at other points in the Newark vicinity. Another possible source of shell lime lies in the loose fossil-shell beds in the vicinity of Salton Sea, Imperial County.

Marl is an intimate mixture of ealcium carbonate and clay in various proportions. The rock may be compact or friable and may be almost any color. Most marl is the result of solidification of limy mud or ooze which has accumulated on a lakebed or on a shallow sea floor, but marl-like deposits sometimes accumulate around hot springs and even about volcanic fumaroles and geysers. Marls are often mixed with shells or shell fragments and if such detritus is abundant the rock should be called shell marl. Marls from the Minkler and Reedley districts have been utilized extensively for agricultural purposes, and smaller marl deposits have been used locally in the vicinity of Lakeside and Jamul, San Diego County; Helendale, San Bernardino County; the Santa Theresa Mountain foothills of Santa Clara County; and Matilija Canyon, Ventura County. Travertine is a more or less banded limestone produced by evaporation of carbonate-laden hot-spring waters. It is commonly composed entirely of calcium carbonate and usually is a dense, compact rock. Travertine seldom accumulates in deposits large enough to permit extensive mining, but one large deposit at Cowell, Contra Costa County, supported a cement plant for many years. Various mixtures of marl and travertine have been mined for agricultural use in Matilija Canyon, Ventura County, from time to time.

Calcareous tufa is a porous, friable, or compact lime rock which is deposited at lake margins and near hot springs, usually in arid regions. The lime is partly precipitated by chemical action and partly by algal organisms. Rather extensive calcareous tufa deposits form weird landscape shapes north of Searles Lake. Invo County, but the material is too remotely situated from arable land to be currently usable as a source of lime. Calcareous tufa has been quarried for agricultural use at Laughlin near Healdsburg, Sonoma County, by the Pacific Lime and Sulphur Company. Calcareous tufa deposits also occur at Mono Lake, Mono County, and Markleeville Creek, Plumas County.

Caliche is a light colored limy or marly accumulation found in superficial deposits in the desert. It may occur as soil impregnation, as thin beds and stringers in alluvium, and as matrix in coarse talus breccia. Some caliche has been utilized for portland cement near Oro Grande, San Bernardino County, but caliches commonly are not extensive enough to be sources of agricultural lime.

Dolomite rock is composed predominantly of the mineral dolomite $(CaCO_3 \cdot MgCO_3)$. There are all gradations between pure dolomite rocks and pure limestones; intermediate varieties termed dolomitic limestone, or limy dolomites depending upon the dominance of one or another of these carbonate minerals. Dolomites closely resemble limestones but are much less soluble in dilute hydrochlorie acid and in most soil acids. Owing to their high magnesium content and their lower solubility in acid solutions, dolomites are less satisfactory than limestone as soil conditioners. As California is well supplied with limestone, it is unlikely that dolomite will be used as an agricultural mineral to any great extent. Dolomite has been used in the eastern states as a substitute for limestone, as a fertilizer filler, and as a soil conditioner.

MINING AND PROCESSING OF LIME MATERIALS

Limestones are mined principally by surface methods in California. Establishment of a quarry entails laying out a level for the quarry floor and driving a face above this level. In some localities it is necessary to work down from the established quarry level or even to resort to underground mining. Two mines in California use underground methods. Subsurface mining of any type is necessarily more expensive than working deposits which lie above a suitable base level. Quarries in very steep terrain are often as unsatisfactory as underground mines because of the necessity of establishing numerous benches or quarry levels or else of operating against daugerous, lofty working faces. Hillside deposits of moderate relief are most satisfactory.

Limestone is blasted from the quarry face to the quarry floor where it is power-loaded onto trucks, railroad cars, or conveyor belts for transportation to processing plants. Primary or coarse-crushing is sometimes accomplished at the quarry and sometimes at the mill by jaw or gyratory crushers. Final crushing at the plant is usually accomplished in a ball mill.

For agricultural purpose, limestone is ground to a variety of sizes. Poultry grit is ground in fairly coarse sizes, but most other agricultural limestone is fine-ground. For use as a soil conditioner, the finer the grind the faster the lime acts. If delayed release is desired, a coarser grind is used. No specifications as to grain size of lime have been set up in California; various manufacturers make different grinds. Searles ¹ states that "any residue left on a sieve having 100 holes per running inch should be regarded as useless to the farmer or gardener as it will not be available in the soil for ten years or more." Recent tests by Greiner ² indicate that this is far too pessimistic a view and that much coarser material is markedly decomposed in some planted soils within a one-year period.

Most marl deposits are worked without use of explosives. They are commonly stripped by bulldozers or power shovels and loaded by power equipment for truck delivery to mill or consumer. Some marls are sufficiently friable to be used without grinding; others are crushed in hammer or ball mills.

Hydrated lime $(CaO \cdot H_2O)$ is the most common form of artificial lime material sold for agricultural purposes. It is usually more finely divided than ground limestone and for that reason is superior to it for some agricultural uses. Quicklime (CaO) is used in small amounts as a disinfectant.

Seashells for agricultural use are dredged from San Francisco Bay by suction dredges, transported to the mill on barges, washed, and then ground in ball mills in much the same fashion as limestone.

AGRICULTURAL USES OF LIME PRODUCTS

By far the largest part of current agricultural lime production is applied to the soil either alone as a conditioner or as a filler in mixed fertilizers. Lime has a number of well known functions in the soil: it acts as a plant food, as a neutralizer of soil acids, as a promoter of growth of certain beneficial bacteria, as a promoter of decay of vegetable matter, and as a deflocculator of clay in "heavy" soils. As most California soils are neither acid nor lime deficient, most lime is applied as a clay deflocculator to increase workability and permeability of elay-rich soils or as a carrier for other fertilizing materials.

Minor uses of lime in agriculture are :

In carbonate form as a source of calcium in stock feed; as seashells, erushed limestone, or dolomite in poultry grit; as lime hydrate in insecticide fruit sprays; as lime hydrate; and as quicklime for disinfectant around livestock corrals and buildings.

More precise data on characteristics, application, and use of lime materials in California may be found in publications of the State Department of Agriculture, particularly those of the Agricultural Experiment Station and the Bureau of Chemistry.

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¹ Searles, A. B., Limestone and its products, p. 548, London, Ernest Benn Ltd., 1935. ² Greiner, Ernst W., Availability by particle sizes: Rock Products, vol. 53, no. 4, pp. 123-125, 160-161, April 1950. Part of a series of articles on marketing of agricultural limestones.

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CALIFORNIA SOURCES OF SULFUR AND SULFURIC ACID

BY JAMES W. VERNON

It is estimated that 125,000 tons of sulfur, elemental and combined, were added to California soils during 1948. Of this amount about 20,000 tons was elemental sulfur, the remainder being in compounds such as sulfuric acid, natural gypsun, aluminum sulfate, copper sulfate, and lime-sulfur. At present California's output of natural sulfur does not exceed 1,000 tons per year, Texas and Louisiana deposits supplying the bulk of the natural sulfur used in the state. Sulfuric acid is essential in the production of most of the manufactured sulfur compounds. Most of the sulfuric acid demands of California are met by acid plants in the state using for raw materials, elemental sulfur, sulfide minerals, and hydrogen sulfide obtained from oil refinery gases. Most of the gypsum used for agricultural purposes in California is produced from deposits in the state.

The only sulfur deposits that have been mined commercially in California in recent years are on the west slope of the Last Chance Range, Inyo County.¹ Here sulfur zones are in a series of limestone breecias. conglomerates, sandstone, and volcanics of Tertiary age. These occurrenees are attributed to the oxidation of hydrogen sulfide gas, or its interaction with sulfur dioxide gas of volcanic origin. The hydrogen sulfide gas necessary for the reactions was derived from gypsum by the action of organic matter and carbonic acid waters. Some sulfur was deposited here by solfatarie action. Lynton, in 1938, conservatively estimated the ore-insight in these deposits to be 253,000 tons containing 40.3 percent sulfur. Total reserves were believed to be approximately 2,500,000 tons of sulfur. Both surface and underground methods have been employed in mining Invo County sulfur. Lack of water in this area has prevented the eoncentration of the sulfur ore, or the application of mining processes similar to those used at the Gulf Coast deposits which involve the use of large quantities of super-heated water.

Small quantities of sulfur have been obtained from gypsum deposits containing 3 to 7 percent sulfur in Imperial County. At the Leviathan mine, Alpine County, sulfur associated with copper represents a potential commercial source.

Most of the minor occurrences of sulfur in California are the result of solfataric action in the vicinity of recent volcanism, or sulfur associated with cinnabar in California's numerous quicksilver deposits. The Sulphur Bank deposits, Lake County, was originally mined for sulfur but it has been principally a quicksilver property.

Production of sulfuric acid in California is centered in the Los Angeles and San Francisco Bay areas. In the bay area, approximately 100,000 tons of pyrite from Shasta County mines are burned annually to produce sulfuric acid. The ores thus used average about 50 percent sulfur. Also, the smelting for metals of sulfide ores from California mines and those of nearby states provides additional material for the production of sulfuric acid.

Pyrite is an iron-sulfide mineral which is widespread in all kinds of rocks and commonly occurs as a gaugue mineral in metallic ore deposits.

¹Lynton, Edward D., Sulfur deposits of Inyo County, California: California Jour. Mines and Geology, vol. 34, pp. 563-589, 1938.

The pyrite being mined in Shasta County occurs as massive replacement deposits in intrusive bodies of alaskite porphyry. The pyrite deposits at the Hornet mine of the Mountain Copper Company, the principal producer, contain more than a million tons of ore averaging 50 percent sulfur. Pyrite is mined here by underground methods. Substantial amounts of pyrite were mined for its sulfur content from Alameda County deposits in the period 1891-1934. In Siskiyou County, large deposits of pyrite occur as irregular replacement bodies and as disseminated grains in a metamorphosed andesite.

Other smaller massive pyrite deposits are known in Mendocino and Santa Clara Counties. Massive sulfide deposits containing principally pyrrhotite, an iron sulfide mineral, in Orange, San Diego, and Trinity Counties also contain substantial reserves of combined sulfur. These deposits represent a potential commercial source of sulfur-bearing material. Small pyrite occurrences of mineralogical interest are known throughout California. Only the deposits of Shasta and Alameda Counties have been exploited for the sulfur in the pyrite.

Hydrogen sulfide gas evolved during petroleum refining is an important source of sulfur for the manufacture of sulfuric acid in Los Angeles and the San Francisco Bay area. The hydrogen sulfide gas is selectively absorbed from refinery gases by use of liquids such as sodium phenolate and diethanolamine. After stripping the hydrogen sulfide from the liquid, the gas is either burned to sulfur dioxide or converted to elemental sulfur.² The Hancock Chemical Company now recovers 50 tons of elemental sulfur per day from oil refinery hydrogen sulfide gas of its plant near Los Angeles.

The sulfur dioxide gas necessary for making sulfuric acid is obtained by burning elemental sulfur, roasting sulfide ores, and from burning hydrogen sulfide gas. Two general types of processes are used to produce sulfuric acid from sulfur dioxide; the nitration and the contact processes. The nitration processes involve the oxidation of sulfur dioxide by oxygen, nitric acid (or higher oxides of nitrogen) in the presence of water. The final reaction products are sulfuric acid and oxides of nitrogen. The contact processes oxidize sulfur dioxide to sulfur trioxide, utilizing platinum, a vanadium oxide, or a vanadium silicate as a catalyst. The sulfur trioxide is subsequently absorbed in concentrated sulfuric acid.

Elemental sulfur is used with calcium hydroxide in the preparation of lime-sulfur solution. The California plants that produce lime-sulfur solution are in Richmond, Port Chicago, El Segundo, and South Gate.

² New California plant makes sulfur from refinery gas: Oil and Gas Jour., vol. 47, no. 51, p. 241, 1949.

CALIFORNIA'S RESOURCES OF THE MINERALS OF MINOR AGRICULTURAL USE

BY LAUREN A. WRIGHT

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INTRODUCTION

Other than fertilizers and gypsum, limestone, sulphur, and sulphuric acid relatively small amounts of mineral substances are used in the beneficiation of California's soils; but of these substances of minor agricultural use, most are readily obtainable from sources within the state. Some of them are applied nearly as they occur in nature and require very simple treatment in preparation for market. Included in this group are the boron minerals, clay, diatomite, peat, pumice, shale, and vermiculite. Of these only vermiculite is not produced commercially in California. Pyrophyllite and tale, mined in the state and marketed as insecticide carriers, are not actually agricultural minerals because they are not used to improve the physical characteristics of the soil or to promote plant growth.

Other minor agricultural minerals used in California are artificially prepared in chemical plants. These include aluminum sulphate, copper sulphate, iron sulphate, manganese sulphate, zinc sulphate, and zinc oxide. Data are not readily available on the raw materials used by many of the chemical plants in California, nor is it known with certainty in what amounts such chemicals are brought into the state and marketed as agricultural minerals. Of the chemicals listed above, however, all except manganese sulphate are produced in California chemical plants.

Most of the materials used as minor agricultural minerals are consumed in much larger quantities by other industries in the state. Regardless of the agricultural demands, therefore, such materials as the boron minerals, elay, diatomite, pumice, shale, and tale can be easily obtained on markets well established by other uses. Conversely, other materials, such as the peat and pyrophyllite mined in California are largely dependent upon the agricultural industries for their markets.

The following discussion is intended mainly as a brief outline of the occurrences and production methods of mineral substances that are used in comparatively small volume in the state's agricultural industries. The natural materials and the products of chemical plants will be considered separately.

BORON MINERALS

Over nine-tenths of the world's output of boron minerals is obtained from the desert regions of eastern and southern California where borates occur as efflorescences on playa lake surfaces, as constituents of lake brines, and as strata in folded Tertiary sediments. The boron minerals currently produced in greatest quantity are kernite $(Na_2B_4O_7 \cdot 4H_2O)$ and borax $(Na_2B_4O_7 \cdot 10H_2O)$. In the past, ulexite $(NaCaB_5O_9 \cdot 8H_2O)$ and colemanite $(Ca_2B_6O_{11} \cdot 5H_2O)$ also were produced in large quantity, but now they are of less commercial importance.

Since 1864 when boron minerals were first recovered in California, they have been obtained successively from several types of deposits. For a period ending in 1872 borax was recovered from lakes in Lake County. During the following fifteen years borax and ulexite were removed from the crusts of playa lakes in the Death Valley and Mojave Desert areas. These operations terminated in the late eighteen-eighties with the discovery of colemanite deposits in folded Tertiary sediments in the Calico Mountains of San Bernardino County. Similar deposits were discovered subsequently in the Death Valley area and in Los Angeles and Ventura Counties. All were worked by underground methods.

Although large reserves of colemanite still remain in some of the deposits mentioned above, very little colemanite has been mined since 1926. In this year large deposits of borax and kernite were opened near Kramer, Kern County. The Kramer deposits, which have proved to be the world's principal borate source, are also in-Tertiary sediments and are likewise worked by underground methods. Significant quantities of borax are also being recovered from the brines of Searles and Owens Lakes as a by-product of operations aimed mainly at the recovery of other saline minerals. In 1948 the output of boron minerals in California totaled about 454,000 tons and was valued at about 11 million dollars.

The boron of commercial borate deposits is believed to have been derived primarily from hot springs or fumaroles associated with Tertiary volcanism. The leaching of hot spring borate deposits in arid regions would ultimately lead to the concentration of boron in the waters of saline lakes and to the precipitation of borates upon the evaporation of such lakes. The Tertiary colemanite deposits of California are generally believed to be folded playa deposits from which sodium borate has been leached from original ulexite. The kernite of the Kramer deposits is believed to have formed by the partial dehydration, through heating, of borax that accumulated in a Tertiary basin.

CLAY AND SHALE

Because of the lack of experimental data the potential significance of California's clay and shale occurrences to its agricultural industry is not entirely clear. Numerous types of clay are mined in California, however, and shale is one of the state's most prominent rock types.

Kaolin minerals, which form the most abundant of the clay mineral groups, are also the most common constituents of the clays mined in California. Among the state's kaolin-rich commercial clays are the fire clays used in the manufacture refractories and in heavy clay products; the china clays used in the manufacture of whiteware, in refractories, and as a filler; and shales and miscellaneous clays used as raw materials in building brick, heavy clay products, and portland cement. Minerals of the montmorillonite group are the principal constituents of both the swelling and non-swelling varieties of bentonite and of fuller's earth. All three occur in commercial quantities in California. The non-swelling bentonite and fuller's earth are used principally as filtering agents in the clarification and decolorization of oils and fats. Of the many uses of swelling bentonites, the principal one is as a constituent of oil well drilling fluids.

Fire elays and china clays are obtained in two general areas in California. One is a narrow, discontinuous belt along the foothills of the central Sierra Nevada. In this belt the principal production centers are at Lincoln and Ione. The second area is at the north end of the Santa Ana Mountains of southern California and centers about the Aberhill district. The clays in these areas and at several other localities in the state formed in early Tertiary time when a warm, moist climate caused a deep weathering of the land surface. Much of the clay produced by such weathering was transported and deposited in lagoons and deltas of an early Tertiary sea. Miscellaneous elays of lower grade are obtained from Recent alluvial deposits at numerous localities throughout the state. Shales exist in unlimited quantities in California, and are particularly abundant in the marine Mesozoic and Cenozoie sediments of the Coast Ranges.

Bentonite and fuller's earth are generally believed to have altered from volcanic rocks. In California these clays are obtained mainly from deposits in the desert regions of the eastern and southern part of the state.

DIATOMITE

Diatomite is a light-weight sedimentary rock composed mostly of the tests of minute siliceous plants known as diatoms. Diatomite is a very porous material, and, when dry, is one of the least dense of all rocks. Although its principal application is as a filtering medium, it is also used extensively as a filler, insulating material, and abrasive. Its application in agriculture is a very minor use.

California contains the nation's most extensive diatomite deposits and is the principal diatomite-producing state. The largest of these deposits have formed as marine sedimentary beds in upper Miocene and lower Pliocene time. In the Santa Ynez Mountains and Santa Maria Basin of Santa Barbara County high-grade diatomite deposits are as much as 1000 feet thick. Other, though smaller, diatomite deposits occur at several localities in the state as fresh-water lake beds of Tertiary and Recent age.

Most of California's large marine diatomite deposits are in the central and southern Coast Ranges. The largest single operation is near Lompoe, Santa Barbara County. Other active deposits of marine origin that are also being worked include another in the Lompoe area; one near Solvang, also in Santa Barbara County; and one in the Palos Verde Hills, Los Angeles County. Fresh-water diatomite deposits are mined at Tionesta, Modoc County, and at Zurich, Inyo County. Most of the diatomite marketed for agricultural use is obtained in relatively small operations in the San Joaquin Valley area.

PEAT

Peat is vegetal matter that has accumulated in lakes and swamps in Recent geologic time. It is composed principally of the remains of such

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materials as mosses, tules, and grasses, and has undergone relatively little decomposition. The commercial types of peat range from a high-grade variety, formed from aquatic mosses and known as peat moss, through sedge or tule peat to peat dirt which is merely soil with a high organic content. Most of the world's output of peat is consumed as fuel; but over nine-tenths of the peat marketed in the United States is used as a soil amendment.

Several thousand tons of peat are produced in California each year. Of this output most is obtained from relatively large deposits of tule peat and peat dirt. But one locality in the state yields the only peat moss mined in the western United States. Most of the peat moss used in California, however, is obtained from out-of-state sources.

The principal peat-producing localities in California are on the delta of the lower San Joaquin and Sacramento Rivers. The state's peat moss output is obtained from a bog in Jess Valley near Likely in Modoc County. Other areas from which peat is obtained in commercial quantities are in Los Angeles, Orange, San Diego, Madera, Fresno, and Siskiyou Counties. Most of the peat mined in California has been removed from the bogs by drag lines. Its treatment has consisted simply of airdrying and shredding.

PUMICE AND PERLITE

Pumice is a light-weight, very porous, volcanic glass formed during the rapid solidification of a siliceous magma. Pumice is thrown from volcanic vents and accumulates in detrital deposits known as tuffs. Pumice deposits are widespread in California but are restricted to areas of Tertiary or Recent volcanism. Pumice is now used mostly as a lightweight aggregate and in smaller, though significant amounts, as abrasive material. It is extensively mined in California principally for these purposes, but as yet only an insignificant amount of this output is marketed as an agricultural mineral.

The active pumice operations in California include several in a volcanic belt east of the Sierra Nevada. Others are in the desert region of southern California, the western foothills of the Sierra Nevada, the Coast Ranges, and in the northeastern part of the state. Most of the state's pumice output is obtained from deposits in Inyo, Madera, Mono, Napa, San Bernardino, Siskiyou, and Stanislaus Counties. All of the pumice currently mined in California is obtained in open-cut operations. In the past, however, some was removed by underground methods.

Strictly defined, the name "perlite" refers to a glassy, volcanic rock capable of breaking down into small concentric-shelled spheres; but in commercial usage the name is applied to any glassy volcanic rock that upon heating will expand into a frothy substance. Such expansible rock is characteristically acidic and contains from 3 to 5 percent water. It ordinarily occurs as layers in thick sections composed of flows and pyroclastic rocks. Like pumice, expanded perlite is used mainly as a lightweight aggregate. Its use as a soil conditioner is minor.

Perlite deposits, although confined to areas of Tertiary or Recent volcanism, are widely distributed in California. They are known to exist at numerous localities in the northeastern part of the state, in the Coast Ranges north of San Francisco Bay, and in the desert region of eastern and southern California. Only two of these deposits are currently active; one near Bigpine, Inyo County, the other near Rutherford, Napa County. 1951]

Both are surface operations. Most of the perlite expanded and marketed in California is brought into the state from Nevada, Arizona, and New Mexico.

PYROPHYLLITE

As previously mentioned, pyrophyllite actually is not an agricultural mineral in that it is not used as a soil amendment. The mineral's chemical inertness and easy grindability, however, has led to its widespread use as an insecticide carrier. Indeed, the mining of pyrophyllite in California is supported mainly by its agricultural use. Pyrophyllite also effectively serves as a filler in numerous substances and as a ceramic raw material.

Pyrophyllite, a hydrous aluminum silicate, has been produced in commercial quantities in California only since 1945. It is currently being mined in three areas, one each in Mono, Inyo, and San Diego Counties. The deposits of Mono County are on the west face of the White Mountains where a 2-mile pyrophyllitic belt forms part of a series of highly metamorphosed pre-Cambrian sedimentary and volcanic rocks. This belt is as much as several hundred feet wide, contains the largest of the state's known pyrophyllite reserves. Not all of the belt, however, is composed of minable material. The Inyo County source is about 5 miles north of Aberdeen and is reported to occur as an altered layer in a Paleozoic sedimentary section. The pyrophyllite mined in San Diego County is obtained from the San Dieguito area where the mineral occurs in lenses that have altered from Jurassic(?) volcanic rocks. Nearly all of the pyrophyllite mined in this area has been obtained from a single pyrophyllite schist mass at least 150 feet long and 10 to 22 feet in outcrop breadth.

The deposits in each of the three areas are mined by open-cut methods. The pyrophyllite is prepared for market by dry-grinding to a size less than 200 mesh.

TALC

The mineral tale closely resembles pyrophyllite in its physical properties, but is a hydrous magnesium silicate rather than a hydrous aluminum silicate. Because tale, like pyrophyllite, is comparably inert and easily ground, it is valued as an insecticide carrier. Only a small fraction of the nearly 100,000 tons of tale now produced each year in California, however, is marketed for this use. Most of the state's tale production is used as raw material in ceramic bodies, as filler, or as paint extender.

The principal tale sources in California occur in a 200-mile belt which is near the state's eastern border and includes parts of Inyo and San Bernardino Counties. Tale deposits in the Inyo Range and its vicinity have formed mostly as alterations of Paleozoic dolomite; but appreciable amounts have also altered from silica rocks and granites. In a region extending from southern Death Valley eastward to the California-Nevada line, extensive tale deposits have formed as alterations of pre-Cambrian carbonate strata at or near the borders of diabase sills. Tale deposits in the Silver Lake-Yucca Grove area are selective replacements of carbonate strata in a highly metamorphosed pre-Cambrian section that has been extensively invaded by granitic rocks. Many of the tale deposits in the Death Valley and Silver Lake-Yucca Grove regions also contain large amounts of the mineral tremolite. MINERALS USEFUL TO CALIFORNIA AGRICULTURE [Bull. 155]

Another extensive talc-bearing belt is in the western foothills of the Sierra Nevada. The tale deposits of this area are associated with serpentine and tale-actinolite schist. Though extensive, they do not contain talc of as high quality as the deposits in eastern California, and their markets have been limited. The Sierran foothill tale, however, has proved suitable for use as an insecticide carrier and several thousand tons of the material are sold each year for this purpose.

Most of the tale mines in eastern California are underground operations, but surface methods have been locally open cuts. The milling of tale, like that of pyrophyllite, simply involves dry grinding to a size less than 200 mesh.

VERMICULITE

The name "vermiculite" is applied to a group of micaceous minerals that expand to several times their volume when heated. They have variable compositions, but all are hydrated silicates. Material marketed as vermiculite commonly also contains the mineral biotite, which, if present in appreciable quantities, will decrease the degree of expansion. The application of expanded vermiculite as a soil amendment stems from its lightness of weight and its ability to hold air and moisture, but the material is used principally as a light-weight aggregate and as an insulating medium.

Vermiculite occurrences in California include localities in Fresno, Riverside, and San Diego Counties; but there has been no recorded commercial production of vermiculite in the state. Large quantities of the material, however, are shipped from a deposit near Libby, Montana, and expanded in California plants. The Montana deposit, which is the nation's principal vermiculite source, has formed by the hydrothermal alteration of an ultrabasic igneous rock.

ALUMINUM SULPHATE

In the preparation of solid aluminum sulphate, finely powdered bauxite, a hydrated aluminum oxide, is dissolved in sulphuric acid and impurities are removed. After the solution is concentrated in a boiler and is allowed to stand for several hours, the aluminum sulphate forms as a white cake.

Aluminum sulphate is manufactured in California at plants in Riehmond and Port Chicago; but the bauxite has been obtained from deposits in the southeastern United States. In mid-1950, when this report was written, the use of foreign bauxite was anticipated. Bauxitic elays in relatively small amounts have been noted at several localities in California, including the Ione area, Amador County, and the Alberhill area, Riverside County; but as yet none of this material has been used in aluminum sulphate manufacture.

Agricultural applications of aluminum sulphate account for only a small part of its total markets. The chemical is used principally in the paper and textile dye industries, and in the purification of water.

COPPER SULPHATE

The copper sulphate produced in California, as well as the world over, is formed by the action of sulphuric acid upon elemental copper. Two plants in the state, one at Richmond and another in Martinez, currently produce copper sulphate. Most of their output is marketed as an insecticide ingredient, and only a very small proportion of it is consumed as an agricultural mineral. The principal raw materials used by these plants are copper precipitates from mine water. These are augmented with scrap copper. The mines from which the precipitates are obtained are in the Iron Mountain area northeast of Redding, Shasta County.

The amount of copper sulphate that has been produced in the state from such precipitates, is insignificant compared to the amount of copper metal obtained from California ores. The state's copper output, which totals more than 600,000 tons is valued second only to that of gold. All but a small amount of this output has been obtained from three districts, one in Shasta County, another in Plumas County, and a third in Sierran foothill counties. Nearly all of these deposits are veins or replacement bodies of copper sulphides in igneous or metamorphic rocks. Although some of the metallic copper produced from California ores has been eventually consumed as scrap in copper sulphate production, the original source of such material is of little significance to the chemical industry.

IRON SULPHATE

Ferrous sulphate is generally a by-product of steel mills, and is produced from waste pickling liquors, which are neutralized with scrap iron, filtered, and concentrated. Crystals of $FeSO_4.7H_2O$ form when the hot, concentrated liquors are cooled. Ferrous sulphate is manufactured at several plants in the Los Angeles and San Francisco Bay areas, but most of them do not offer the material on the open market.

One company, which operates a ferrous sulphate plant in Richmoud, does market its product. In this operation scrap iron is dissolved in sulphuric acid, the liquid is concentrated, and hydrous ferrous sulphate forms. In mid-1950 this company planned to convert to the use of pickling liquid imported from the eastern United States. At that time also, the same company had recently constructed a plant to produce anhydrous ferric sulphate. This plant uses iron oxide cinders, derived from the roasting of pyrite in the production of sulphuric acid, and combines them with sulphuric acid. The pyrite is obtained from deposits at Iron Mountain northeast of Redding in Shasta County.

ZINC SULPHATE

Because of low demands, relatively small amounts of zine sulphate have been produced in California; but plants in both the San Francisco Bay area and Los Angeles area have manufactured this material. These generally employ by-product, zine-bearing substances, and obtain them from various smelters throughout the western United States. Zine dross has been imported from Kellogg, Idaho. Densified fume dust has been obtained from this source and from Tooele, Utah. Roasted zine concentrates have been shipped from Amarillo. Texas. Most of the zine sulphate now produced in California uses various by-products obtained from the manufacture of spelter at a plant in Torrance, California. In the manufacture of zine sulphate, zine is dissolved in sulphurie acid; the solution is purified and evaporated to produce hydrous crystals. Although zinc-bearing ores have been mined at numerous localities in California, about half of the state's total zinc output was obtained during World Wars I and II. The current production is but a small fraction of the national total and is shipped to out-of-state smelters. The nearness of zinc deposits, therefore, is currently of little economic significance to plants producing zinc sulphate in California.

Most of the state's zinc output is now obtained from mines in Inyo County where zinc and lead minerals occur in close association. These deposits are veins or replacement bodies in Paleozoic carbonate sediments. In the past, relatively large quantities of zinc were obtained as a by-product of the previously mentioned copper mines, in the Sierran foothills, and in Plumas and Shasta Counties.

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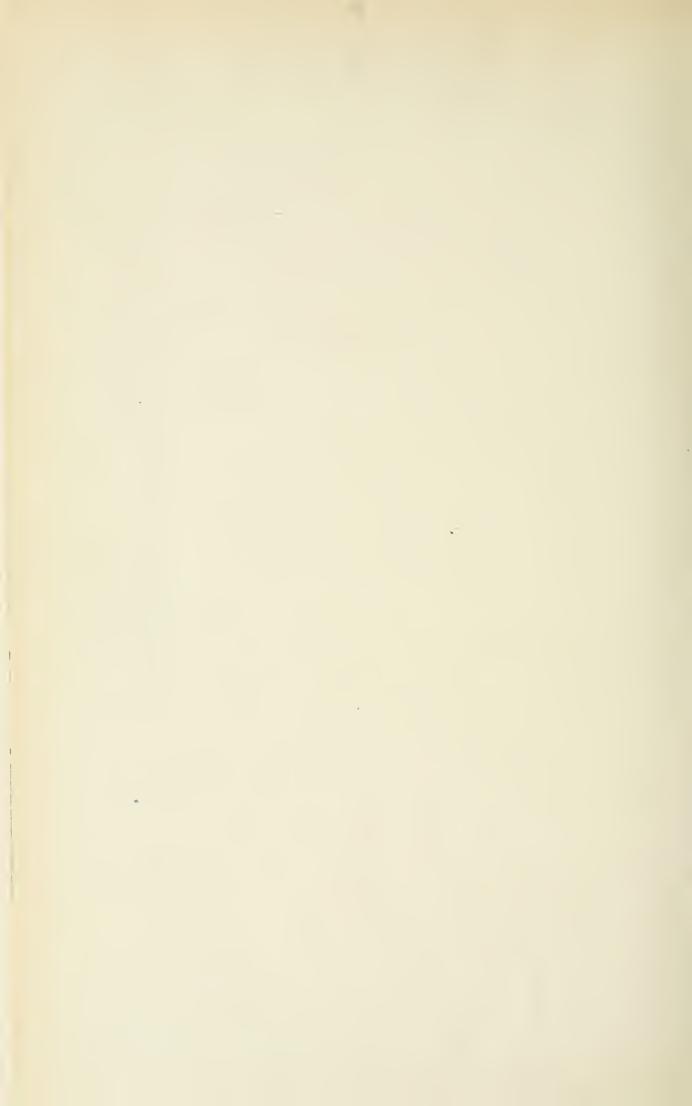
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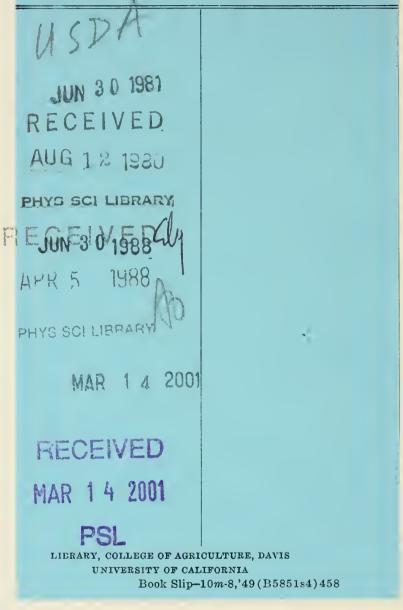
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